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THE EFFECTS OF ELECTRON BEAM IRRADIATION ON ADDITIVES PRESENT IN FOOD-CONTACT POLYMERS

BY

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A CROWSON

ABSTRACT

A range of additives (Irganox 1010, Irganox 1076, Irganox 1330, Irgafos 168 and Tinuvin 622) has been incorporated into a variety of food-contact polymers including polypropylene and low density polyethylene. Samples of these stabilized polymers were subjected to electron-beam or gamma irradiation to receive doses of 1,5,10,25 and 50 kGy.

The effects of electron-beam irradiation on the amount of extractable antioxidant in polymers were determined. Using hplc techniques it was found that there was a dose-related reduction in the amount of extractable antioxidant similar to that caused by gamma irradiation. The magnitude of this reduction was found to be dependent upon the nature of both the antioxidant and the polymer type.

Electron-beam irradiation was also found to cause a dose-related reduction in the levels of the antioxidants Irganox 1010 and Irganox 1076 migrating from polymers into a food simulant. This effect was similar to that caused by gamma irradiation.

The extent of polymer binding of antioxidant fragments derived from Irganox 1076 following electron-beam irradiation was determined, using a radiochemical method. The amount of binding was found to be dose-related and of a similar order of magnitude to that caused by gamma-irradiation.

This study has revealed the presence of many irradiation derived antioxidant transformation products in extracts from irradiated polymers. Attempts have been made to isolate and identify these compounds, and a number of possible structures are proposed following lc-ms studies. In some cases, the irradiation-derived transformation products appear to be different to those produced on thermally aging stabilized polymers. Irradiation was also found to give transformation products formed via the cleavage of tertiary butyl groups from the parent molecules, and such compounds are not produced during the thermal aging of similar stabilized polymers, nor in model reactions between the antioxidants and t-butylperoxyl radicals.

A brief examination of the effects of gamma irradiation on Tinuvin 622 in polypropylene was also carried out, and a number of UV absorbing transformation products were detected.

CONTENTS

CHAPTER 1 - INTRODUCTION

1.1 FOOD IRRADIATION

The amount of food spoilage caused by infestation, contamination and deterioration is enormous worldwide and particularly large in developing countries.[1] With a rapidly expanding world population, any preventable loss of food is intolerable. In addition, foodborne disease is one of the most widespread threats to human health and an important cause of reduced economic productivity.[1] Various methods of preserving food have been used over the years to combat this problem, including salting, cooking, drying, fermentation, smoking, canning, freezing and chemical preservation. Each of these methods has both advantages and disadvantages. The treatment of food with ionizing radiation is the most recent addition to this list. Irradiation can retard food spoilage, reduce insect infestation and reduce contamination from organisms such as bacteria, moulds and yeasts which may cause foodborne diseases. It is also effective in lengthening the shelf-life of fresh fruits and vegetables by controlling the normal biological changes associated with ripening, maturation, sprouting and aging. However, there are some problems with irradiation in that some foods are softened by it and it can produce an undesirable flavour in others.[1]

The public has been rather less than enthusiastic about the use of food irradiation [2], perhaps because they

confuse irradiation with radioactive contamination. The London Food Commission have been particularly vehement in their opposition.[3] However, at the doses of irradiation used for the treatment of food there is no possibility of inducing radioactivity.[1] In addition to this, none of the studies which have been carried out by the FAO, IAEA or WHO showed any indication that food irradiated at or below 10kGy contained radiation-produced carcinogens or other toxic substances.[1]

The treatment of food using irradiation offers some unique advantages over conventional methods, in particular it provides the opportunity to treat foods after packaging. This prevents microbes in untreated foods from contaminating food that has already been processed.[4,5] Food irradiation can also be combined with other food treatment techniques. The effects of this may be better than those produced by either of the processes when used separately.[6]

1.1.1 HISTORY OF FOOD IRRADIATION

The irradiation of food is not a new technique; Swedish scientists first irradiated strawberries in 1916. The development of economic ways of producing ionizing radiation, in the amounts needed for industrial food processing, in the early 1940's provided the next research impetus.[1] However, the possibility of using ionizing radiation for food preservation has only received serious attention over the last thirty years.[7] In 1982 the UK

Government set up the Advisory Committee on Irradiated and Novel Foods (ACINF) to review the evidence on the safety and wholesomeness of irradiated food. The recommendation of this committee was that irradiation of food up to an overall average dose of 10kGy presents no toxicological hazard and introduces no special nutritional or microbiological problems.[6] Following this recommendation the Food Bill, which has recently passed through parliament, permits food irradiation in accordance with strict legislative controls. In fact, the first licence to irradiate food in Britain has recently been granted to Isotron PLC of Swindon. The licence is valid for three years and for the treatment of dried herbs and spices. The packaging materials which are permitted to be in contact with the spices at the time of irradiation are paper, cardboard, polypropylene and polyethylene.

1.1.2 IRRADIATION TECHNIQUES

The cost effective irradiation of food can be achieved using two main types of ionizing radiation. Firstly, via the exposure of food to the radiation arising from radionuclides which produce gamma rays. One radionuclide that is readily available in large quantities is cobalt-60, which is produced by exposing naturally occuring cobalt-59 to neutrons in a nuclear reactor. The use of caesium-137 is also a possibility. However, caesium-137 is a by-product of nuclear reactor operations and not readily available. Gamma rays from either of these radionuclides

will penetrate deeply enough to meet virtually all food irradiation needs. Secondly, machines such as electron accelerators may be used as the source of ionizing radiation. This is a cheaper option; however, accelerated electron-beams can only penetrate food to a maximum depth of about 8cm, which may not be sufficient in some cases. Electron accelerators have the advantage that they can be switched on and off at will, unlike radionuclide sources. They are also more amenable to on-line processing techniques. Electron accelerators also have the advantage that a very high dose rate of several tens of kGy per second is possible which is much faster than gamma irradiators (which deliver typically 12kGy per hour).
Both of these sources can be used for batch or continuous type plants, but they must be installed in a shielded cell specially designed to prevent exposure of personnel to radiation.

1.1.3 EFFECTS OF IRRADIATION ON MATTER

Charged particles such as electrons of moderate energy interact with matter largely through the coulomb forces between them and the orbital electrons of the atoms of the absorber. This causes excitation or ionization to occur in the absorber atoms. These processes may be repeated many times in the absorber until all the kinetic energy of the incident electron is dissipated and the incident electron is captured by a cation.[10]

In addition to loss of energy through excitation and ionization, electrons can lose energy through two other processes, Bremstrahlung and Cerenkov radiation. Bremstrahlung production is appreciable only with electrons having energies above 1MeV. While the Bremstrahlung that may be produced in food is of insufficient quantity to cause significant chemical change, it may induce radioactivity if the energy level is sufficiently high. This is the principal reason for the need to limit the energy level of electron-beams used in food irradiation. Cerenkov radiation has no meaningful role in food irradiation.[10]

Electromagnetic irradiation, such as gamma rays can interact with matter in three different ways, photoelectric absorption, Compton scattering and pair production. The type of interaction depends upon the irradiation energy and the atomic numbers of the atoms making up the material.

Photoelectric absorption involves the gamma photon transferring all its energy to an orbital electron of the material. Photoelectric absorption is the most important interaction for high atomic number elements and irradiation energies of less than 0.1MeV. In Compton scattering, part of the energy of the incoming gamma ray is transferred to an orbital electron, whereupon the orbital electron and the de-energised beam of irradiation move away in different directions. Compton scattering is the most important interaction for low atomic number elements and higher irradiation energies. Pair production

occurs when a very high energy irradiation beam interacts with the field of a nucleus and produces a positron electron pair. It is pair production that induces radioactivity.

In packaging materials which contain mostly light elements such as C, H, N, O and Cl, the gamma irradiation energies appropriate to food processing cause predominantly Compton scattering to occur.

The interactions of irradiation with matter are more fully discussed by Gopal and Urbain.[9,10]

1.1.4 DOSE MEASUREMENTS

The most critical factor in food irradiation is the dose of radiation administered. For each different kind of food, a specific dose has to be delivered to achieve a desired effect. If the amount of radiation delivered is less than the appropriate dose, the intended effect may not be achieved. Conversely, if the dose is excessive the food product may be so damaged as to be rendered unacceptable.[1,11]

The S.I. unit for the measurement of absorbed dose is the Gray (Gy). It is defined as the mean energy imparted by ionizing radiation to matter per unit mass. One Gray is equal to the absorption of one joule per kilogram. Various types of dosimeter are used to measure the irradiation dose absorbed by materials. The need for dosimetry and the various types of dosimeter available have been reviewed elsewhere.[11-14] Dosimetry must be used in the

commissioning of irradiation facilities, the validation of the treatment procedures and in process control.

1.1.5 DETECTION METHODS

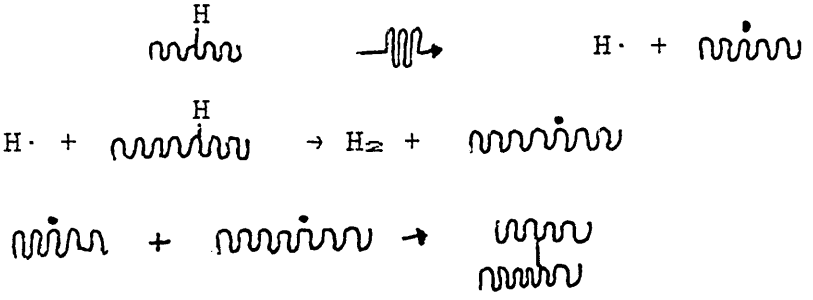
In order to enforce the relevant legislation, to prevent abuses and to ensure public safety, a method of detecting food which has been irradiated is required. The need for such a test and the role it would fulfil have been discussed by Swallow.[15] Various possible tests have been reviewed by Delincée and Ehlermann.[16]

1.2 EFFECTS OF IRRADIATION ON POLYMERS

The packaging of food facilitates its transport, storage and utilisation. It can also keep food in sterile conditions thus improving its quality.[17] One specific advantage of food irradiation is the unique possibility of treating foods after packaging. In view of the importance of cross contamination in the food industry, this is of great value.[1,5,18] The most commonly used materials for food packaging are organic polymers such as polypropylene and polyethylene. These materials can protect the product from the effects of oxygen, light and microorganisms. They can also prevent dehydration and the loss of flavour components.[17] If irradiation of pre-packaged foods is to be used safely then a knowledge of the effects of irradiation upon these polymers is of great importance.[19,20]

Irradiation in vacuo can induce four types of reaction in polymers:

i) CROSSLINKING:- Crosslinking is initiated by the irradiation removing a hydrogen atom from the polymer chain, resulting in the formation of a polymeric radical. The hydrogen atom may then abstract another hydrogen from a neighbouring polymer molecule, resulting in the production of a further polymeric radical. The two polymeric radicals then combine forming a crosslink. This process results in the formation of a three-dimensional crosslinked network and an increase in the average molecular weight of the polymer. A decrease in its solubility in organic solvents is a result of this. The process is represented below :



ii) DEGRADATION:- In this process irradiation results in the breaking of bonds along the polymer backbone to produce two polymeric radicals and subsequently molecules. This process causes a decrease in the average molecular weight of the polymer.

iii) FORMATION OF UNSATURATION:- If two substituent groups on adjacent carbon atoms of the polymer backbone are removed by irradiation then unsaturation will result.

iv) FORMATION OF VOLATILE PRODUCTS:- When some of the above reactions involve terminal alkyl groups, low molecular weight, volatile, hydrocarbons can be produced. Hydrogen can also be released.

Irradiation in air results in oxidative degradation of the polymer taking place. This process is similar to that occurring in the polymer when it is subjected to thermal processing in air and is outlined in table 1.1.[21]

TABLE 1.1

Radiation induced polymer radical reactions

INITIATION $RH \xrightarrow{\sim} R\cdot + H\cdot$

POLYMER RADICAL OXIDATION REACTIONS

$$R\cdot + O_2 \rightarrow RO_2\cdot$$

$$RO_2\cdot + RH \rightarrow ROOH + R\cdot$$

$$ROOH \rightarrow RO\cdot + HO\cdot$$

$$RO\cdot + RH \rightarrow ROH + R\cdot$$

$$HO\cdot + RH \rightarrow R\cdot + H_2O$$

RADICAL REACTIONS DURING IRRADIATION

$$RO_2\cdot \xrightarrow{\sim} R\cdot + O_2$$

$$R'RO_2\cdot \xrightarrow{\sim} R\text{-}CHO + R'O\cdot$$

$$R'ROOH \xrightarrow{\sim} R'RO\cdot + HO\cdot \rightarrow RC{=}O + R'\cdot + HO\cdot$$

$$R'ROOR \xrightarrow{\sim} R'RO\cdot + RO\cdot \rightarrow RC{=}O + R'\cdot + RO\cdot$$

TERMINATION REACTIONS

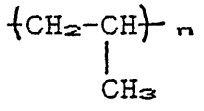
$$R\cdot + R\cdot \rightarrow R\text{-}R$$

$$2RO_2\cdot \rightarrow ROOR + O_2$$

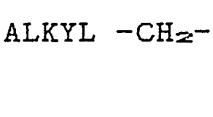
As indicated in the table, this process also results in the formation of volatile compounds such as carboxylic acids and aldehydes. These compounds can cause problems in food-contact applications since they result in taint. The relative importance of these reactions is dependent upon the polymer type. During this project two basic types of polymer have been used, polypropylene and polyethylene. The effects of irradiation on these particular polymers are discussed below.

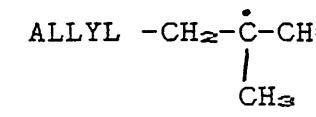
1.2.1 POLYPROPYLENE

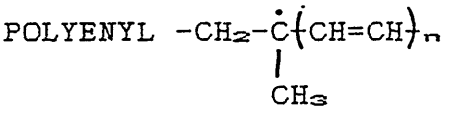
Polypropylene is a nonhomogeneous semicrystalline polymer and to a first approximation can be considered a two phase system consisting of amorphous and crystalline domains. The degree of crystallinity ranges from 0.35-0.65.[21] It has the following chemical structure :-



Although radicals are formed throughout the polymer upon irradiation, radiation induced oxidation of polypropylene occurs almost exclusively in the amorphous phase.[22] This is due to the fact that diffusion of radicals, oxygen and stabilizers is limited to the amorphous regions at temperatures below the melting point of the polymer.[23] When irradiation of polypropylene takes place in vacuo, three radical species are formed:

ALKYL 

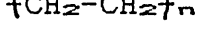
ALLYL 

POLYENYL 

Of these species the alkyl radical is dominant. However, in the presence of air peroxy, and alkoxy radicals are also formed, but not at very high concentrations. Increasing the dose to which the polymer is subjected increases the build up of peroxides.[24] When the irradiation is carried out in air, degradation is the prominent process in polypropylene rather than cross-linking which is predominant in vacuo.[25]

1.2.2 POLYETHYLENE

Polyethylene is a branched, nonhomogeneous semicrystalline polymer. It can also be considered a two phase system. The amorphous phase contains a large number of both long and short branches. The crystallinity occurs in the segments of the chain between branches. It has the following chemical structure :-



Polyethylene is available commercially in a number of forms of which two have been used during this project, low density and linear low density. Low density refers to a lower degree of crystallinity of about 0.55 which makes

the polymer more susceptible to oxidative degradation than high density polyethylene which has a degree of crystallinity of about 0.9. Linear LDPE will be slightly more crystalline since it has fewer branches. As with polypropylene radiation induced oxidative degradation is restricted to the amorphous phase.[26] When irradiated in air, polyethylene is more likely to undergo crosslinking than polypropylene especially at doses of 50kGy or more.[26] Below 50kGy degradation occurs in a similar manner to that described earlier.

1.3 POLYMER ADDITIVES

Pure polymers are susceptible to aging and decomposition by both heat and light. This affects both their physical and chemical properties. Thus, in order to allow processing and subsequent utilisation of polymers in many different applications, additives are added to counteract this problem. The additives incorporated into polymers may, for example, be :

Antioxidants
Light stabilizers
Plasticisers
Antistatic agents
Slip additives
or Antacid agents

Antioxidants are particularly important in polymer formulations since they help to prevent oxidative decomposition of the polymer caused by heat or light. In this present study, polymers containing four different

antioxidants have been used. The chemical structures of these antioxidants are shown in figure 1.1 and their trade and chemical names are given below.

IRGANOX 1010
- [tetrakis (methylene 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate) methane]

IRGANOX 1076
- [octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate]

IRGANOX 1330
- [1,3,5-trimethyl-2,4,6-tris(-3',5'-di-t-butyl-4-hydroxybenzyl) benzene]

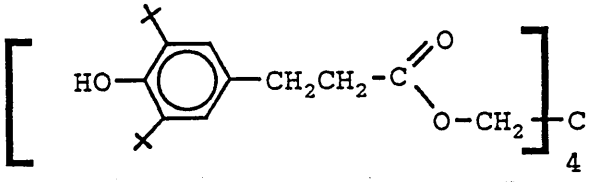
IRGAFOS 168
- [tris (2,4-di-t-butylphenyl) phosphite]

Hindered Amine Light Stabilizers (HALS) are also being used increasingly in polymer formulations. In this present study polypropylene containing the HALS Tinuvin 622 has been used. Tinuvin 622 is a polycondensate of N-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine with succinic acid, its structure is given in figure 1.2.

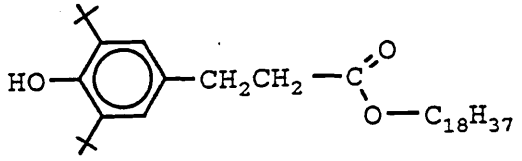
FIGURE 1.1

CHEMICAL STRUCTURES OF ANTIOXIDANTS

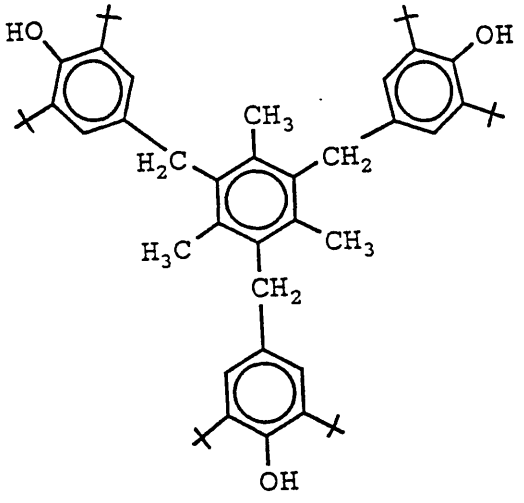
IRGANOX 1010 (RMM = 1178)



IRGANOX 1076 (RMM = 530)



IRGANOX 1330 (RMM = 774)



IRGAFOS 168 (RMM = 646)

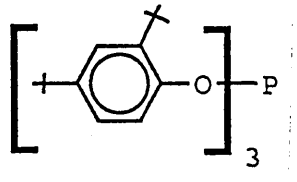
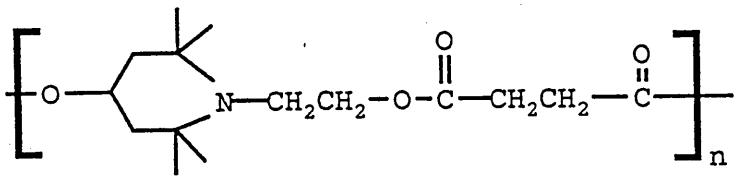


FIGURE 1.2

CHEMICAL STRUCTURE OF TINUVIN 622



1.4 ANTIOXIDANTS: THEIR MODE OF ACTION AND TRANSFORMATION PRODUCTS

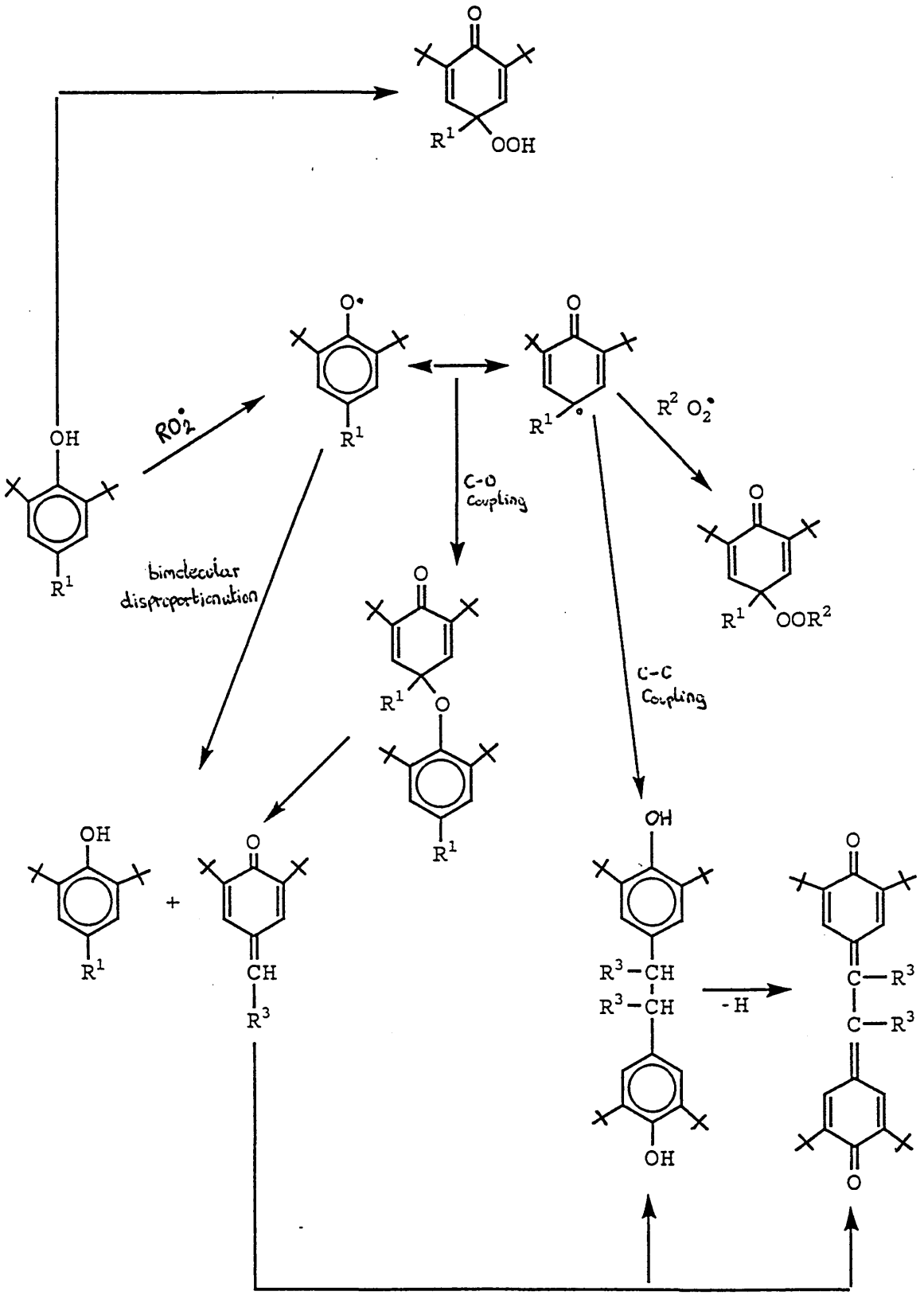
As outlined in section 1.2, polyolefins are susceptible to oxidative degradation. This ultimately leads to a loss of physical integrity. This process can be initiated by thermal processing (processing temperatures are usually in the range 170-280°C, whilst end-use temperatures will usually be much lower), exposure to light or by treatment with ionizing radiation, as long as oxygen is present.

It follows that, if polyolefins are going to be of long term use and widely applicable, some method must be found to retard this degradation process.

From table 1.1 it is evident that it is possible to retard the degradation by removing oxygen, alkyl radicals, alkoxy radicals or alkylperoxy radicals from the system.

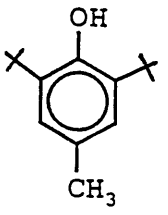
Hindered phenol antioxidants are able to fulfil this role, interrupting the chain of degradative reactions. They are thus referred to as chain-breaking antioxidants. These compounds have been the focus of intensive industrial and academic research for about the last 35 years.[27] Pospisil has proposed reaction scheme 1 [27] for the mechanism of antioxidant action of such hindered phenols.

SCHEME 1

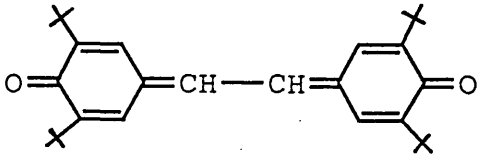

OOH
OH
$RO_2^{\bullet}$
C-O Coupling
$R^2 O_2^{\bullet}$
bimolecular disproportionation
C-C Coupling
OOR^2
-H

It is important to note that the products formed in this scheme cannot be considered to be inert compounds from the point of view of the thermal or photo-oxidative stability of polymers. These products may well undergo further reactions, some of which will be of value in stabilizing the polymer, to yield other compounds.[27,28]

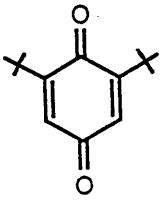
The first commercially important phenolic antioxidant to be used was butylated hydroxytoluene (BHT) (2,6-di-t-butyl-4-methylphenol).



The mechanism of action of BHT has been studied in some detail and is reviewed elsewhere.[28-32] Reactions of BHT are known to result in the production of a number of compounds including a stilbene quinone (I) and 2,6-di-t-butyl-benzoquinone (II).



(I)



(II)

In fact 2,6-di-t-butylbenzoquinone is an almost universal product of oxidative transformation of phenolic antioxidants of the type used during this study.

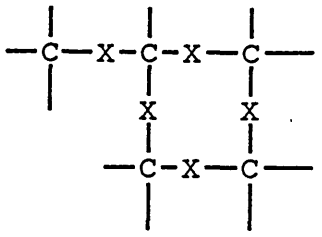
However, BHT is gradually being replaced since it is rapidly lost during processing and weathering because of

its high volatility [33] making it unable to confer long term stability upon polymers. Thus many higher molecular weight, less volatile, phenolic antioxidants, including Irganox 1010, Irganox 1076 and Irganox 1330 have been synthesised. These antioxidants offer much better long term stability for polymers.

Although reaction schemes, such as scheme 1, have been proposed, studies concerning particular antioxidants are sparse and there are relatively few which suggest structures for the many transformation products produced during their action.[28,30] Due to the more complex structures of these high molecular weight phenols BHT cannot necessarily be considered an adequate model for them.

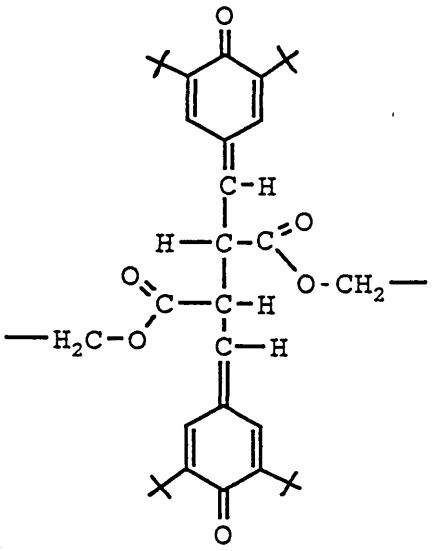
The literature relevant to Irganox 1010, Irganox 1076 and Irganox 1330 is reviewed below. Details of some model reactions, which may produce similar compounds to those produced during the action of antioxidants in polymers, are also included. The difficulties involved in analysing and characterising antioxidant transformation products are widely recognised. The process is both time and labour-intensive.

In the case of Irganox 1010 only two model reaction studies appear to have been carried out. Firstly, Irganox 1010 was oxidised using potassium hexacyanoferrate(III) under alkaline conditions by Duynstee.[34] This procedure produced a yellow powder for which a crosslinked polymeric structure was suggested (III).

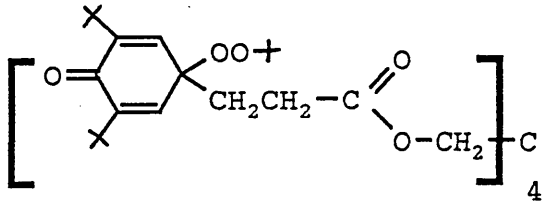


(III)

where X =

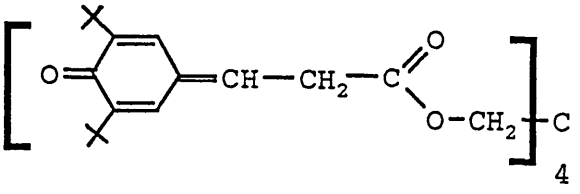


Secondly, Kovárová-Lerchová and Pospisil [35] have carried out a study of the reaction of Irganox 1010 with t-butylperoxyl radicals generated catalytically from t-butylhydroperoxide which models oxidised polypropylene. This reaction resulted in the production of tetrakis [methylene-3-(1-t-butylperoxy-3,5-di-t-butylcyclohexa-2,5-di-ene-4-onyl) propionate] methane (IV).



(IV)

Henman [28] has examined the antioxidant behaviour of a quinone methide derivative of Irganox 1010 (V).

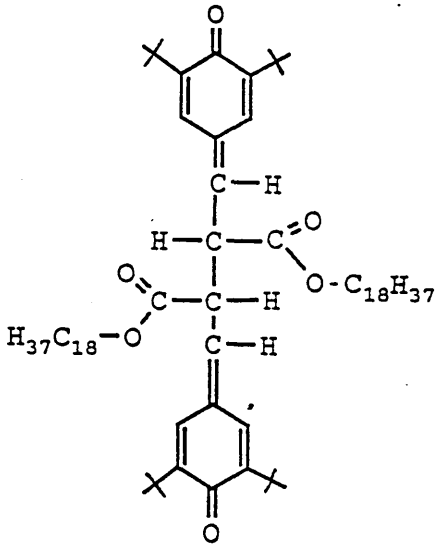


(V)

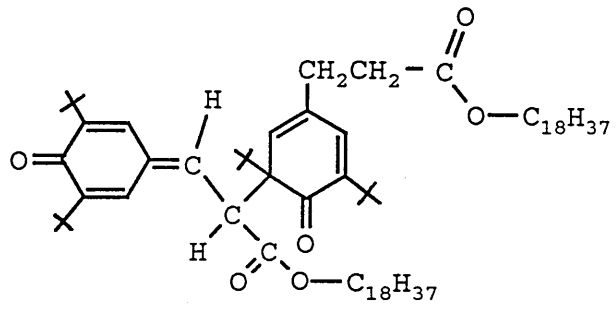
Some thermal aging experiments at 150°C in air have been carried out by Frank [36] on polypropylene stabilized by Irganox 1010. Although at least two transformation products were detected, they were not identified. The UV spectra of two of these compounds showed different absorbance maxima at 280nm and 320nm respectively. This suggests that the first one retains phenolic character whilst the second has a conjugated, possibly quinonoid type structure.

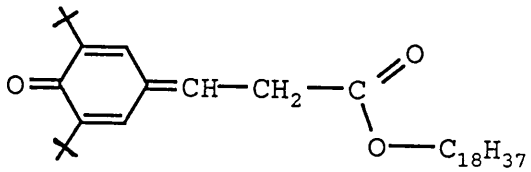
More work has been carried out on the transformation products of Irganox 1076. Irganox 1076 has also been oxidised using alkaline potassium hexacyanoferrate(III) to yield a dimeric compound (VI) which has two diastereoisomers. [34,37,38]

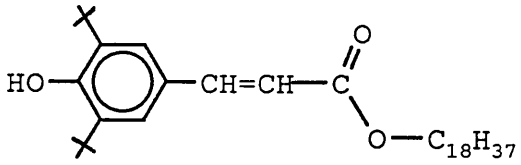
(VI)



This reaction is known to proceed via three intermediates (VII, VIII, IX).

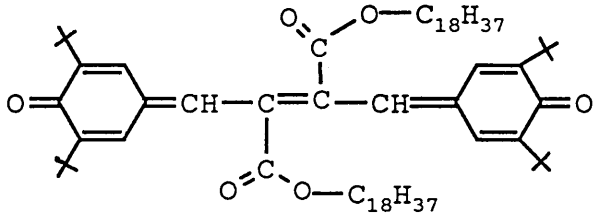
(VII) 

(VIII) 

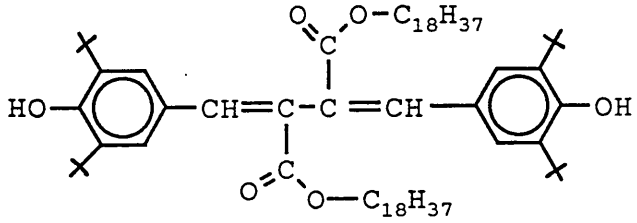
(IX) 

Samsonova *et al* [39] also suggested that other products of Irganox 1076 can be produced (X, XI), although this was not confirmed. These workers also reported a photo-oxidative method for producing compound XII.

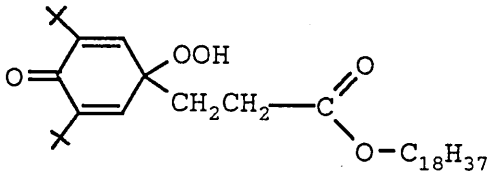
(X)



(XI)

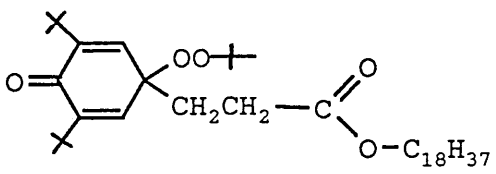


(XII)

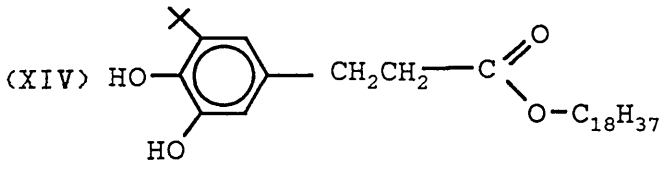


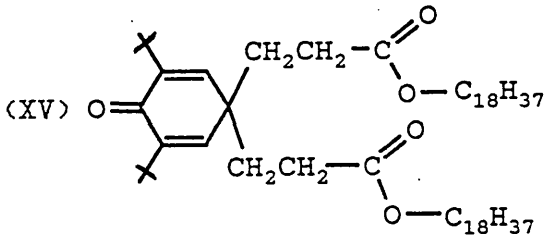
In addition they also carried out a model reaction between Irganox 1076 and t-butylperoxyl radicals generated from t-butylhydroperoxide using a cobalt (II) acetyl acetonate catalyst. This produced a molecule similar to XII, XIII, together with other deeply coloured compounds which were not identified.

(XIII)



Duynstee [34] subjected compound XIII to thermal decomposition (80 minutes at 140°C) which resulted in the production of at least 12 different products some of which remain unidentified. He suggests that the products include Irganox 1076, 2,6-di-t-butylbenzoquinone and compounds VI, XIV and XV.



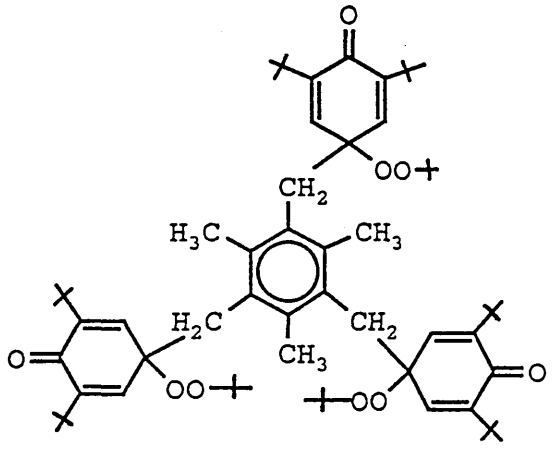


A reaction of particular importance for the present study was the treatment by Duynstee [34] of polyethylene stabilized by Irganox 1076 in a Brabender plastograph for two hours at 200°C in the presence of oxygen. This process was found to produce at least twelve different transformation products including VI, VIII, and XIV. A poster presented by Jonas *et al* [40] describes the oxidation of Irganox 1076 using five different methods. The compounds produced were analysed using a reversed phase HPLC technique and a multichannel UV/VIS detector. The details of this method are not included. The oxidation methods were as follows :

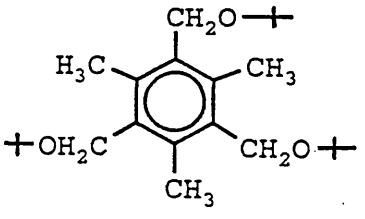
- Alkaline $K_3Fe(CN)_6$ at 60°C
- PbO_2 in cyclohexane at 20-80°C
- air at 160-200°C for up to 72 hours
- 0.1% in MDPE processed at 200°C in a Brabender plastograph
- 0.1% in 1.5mm thick MDPE plaques at 110°C

Extraction of the polymers was carried out by heating at 80°C in 1,2-dichloroethane for four hours. Six transformation products were identified, although the means of identification is not detailed. These compounds were VI (both diastereoisomers), IX, X, XI and a phenol/quinone dimer. It is not entirely clear which of the oxidation processes produced which products.

Most of the work concerning Irganox 1330 has been carried out by Koch.[41-43] He reports that the reaction between Irganox 1330 and t-butylperoxyl radicals produces compound XVI, which decomposes on heating to give compound XVII and 2,6-di-t-butylbenzoquinone.[41]



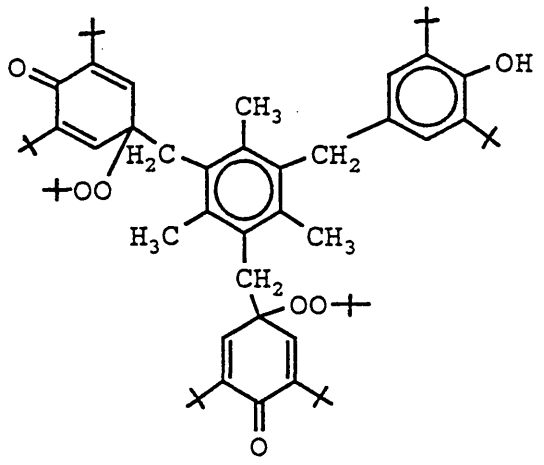
(XVI)



(XVII)

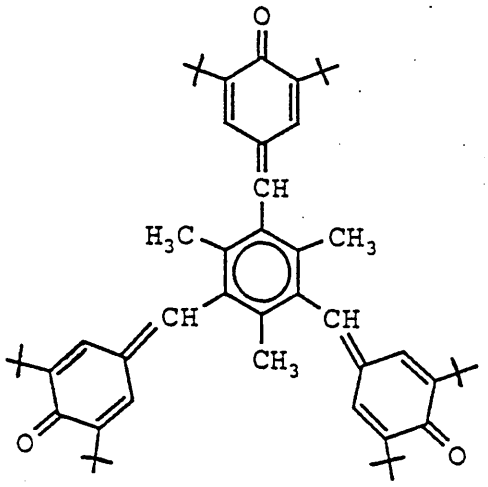
Some similar work to this was carried out by Lerchová and Pospisil.[44] They were able to isolate the partial oxidation product compound XVIII.

(XVIII)



They report that the UV spectrum of XVIII has a weak absorption in the range from 260 - 330nm with an unpronounced maximum at 275nm. Along with compounds XVI and XVIII, a brown mixture of other compounds was formed from oxidising Irganox 1330. These compounds remain unidentified. Koch also reports that atmospheric oxidation of Irganox 1330 at 230°C produced compound XIX along with 3,5-di-t-butyl-4-hydroxybenzaldehyde and 2,6-di-t-butylbenzoquinone.

(XIX)

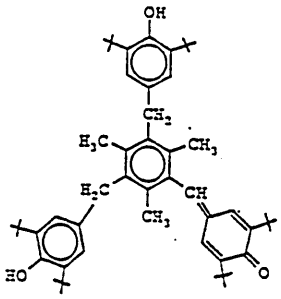


The UV spectrum of compound XIX is reported to have an absorbance maximum at 334nm.[41]

Koch also carried out thermal processing at 200°C in air of polypropylene stabilized by Irganox 1330. Thirteen transformation products in the polypropylene subjected to this procedure were identified using mass spectrometry (figure 1.3).[42]

FIGURE 1.3

TRANSFORMATION PRODUCTS OF IRGANOX 1330 STABILIZING POLYPROPYLENE PRODUCED BY THERMAL PROCESSING



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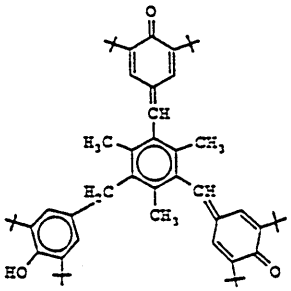

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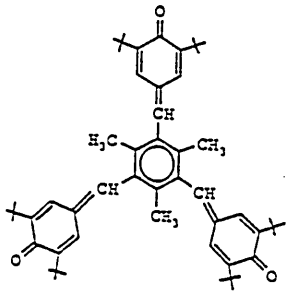

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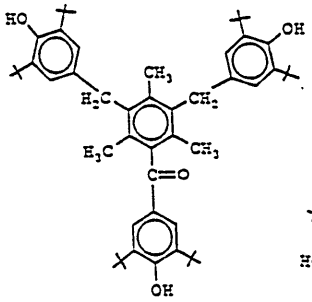

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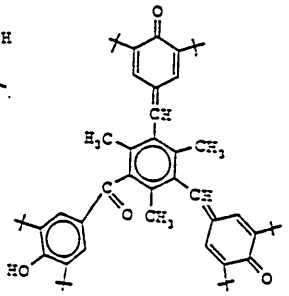

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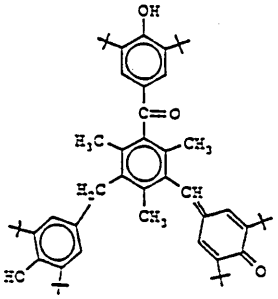

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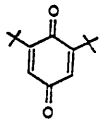

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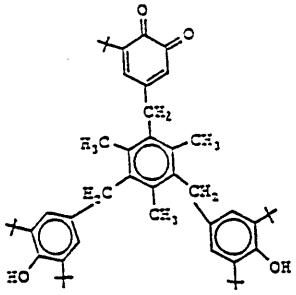

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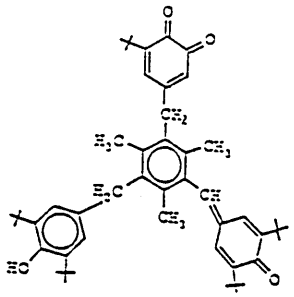

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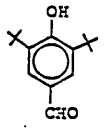

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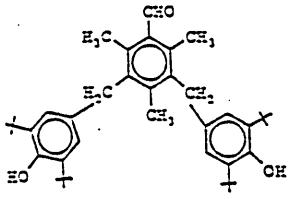

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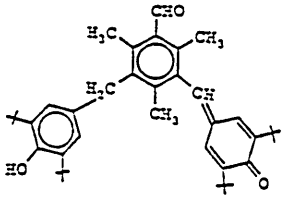

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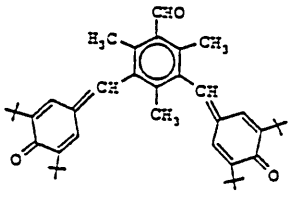


RMM = 580

Additionally the amount of binding to the polymer was investigated. Polypropylene containing ^{14}C labelled Irganox 1330, with the label at the benzylic positions, was kneaded in air at 200°C for 50 minutes and then exhaustively extracted with trichloromethane. The amount of activity remaining bound to the polymer was 41%.[43] This is one of the few pieces of work to actually prove that polymer binding takes place in these situations.

It is clear from the experiments detailed above that there is still a great deal to be discovered about the transformation products of such antioxidants. In addition there appear to be few literature references, other than those written by workers at Sheffield City Polytechnic[45-61] about the effects of ionizing radiation on antioxidants stabilizing polymers.

Another class of compounds which are able to act as chain-breaking antioxidants are the sterically hindered aryl phosphites such as Irgafos 168. These compounds can also act as hydroperoxide decomposers further interrupting the oxidative degradation of polymers. They undergo the following reactions[52,56] :-

$$ROO\cdot + P(OAr)_3 \rightarrow ROOP\cdot(OAr)_3 \rightarrow RO\cdot + O{=}P(OAr)_3$$

$$RO\cdot + P(OAr)_3 \rightarrow ROP\cdot(OAr)_3 \rightarrow ROP(OAr)_2 + ArO\cdot$$

$$\searrow$$

$$R\cdot + O{=}P(OAr)_3$$

$$ROO\cdot + ArO\cdot \rightarrow \text{inactive products}$$

$$ROOH + P(OAr)_3 \rightarrow RO^- + HOP^+(OAr)_3 \rightarrow ROH + O{=}P(OAr)_3$$

Only those phosphites which react by substitution to give free aryloxyl radicals are effective chain-breaking antioxidants.[55] They show a more than additive increase in stabilizing action when mixed with phenols and are therefore widely used. There is little known about the nature and role of their transformation products.[54] Again there appear to be no literature references other than those written by workers at Sheffield City Polytechnic [46,48,49] about the effects of ionizing radiation on aryl phosphites stabilizing polymers.

It is important to note that polymers are often stabilized by using a synergistic mixture of antioxidants. This complicates the situation even further, as indicated by work carried out by Duynstee [34] involving oven aging of polypropylene stabilized with a mixture of Irganox 1076 and Irgafos 168. The use of such combinations opens up the possibility of reactions between the different antioxidants and also between their respective transformation products.

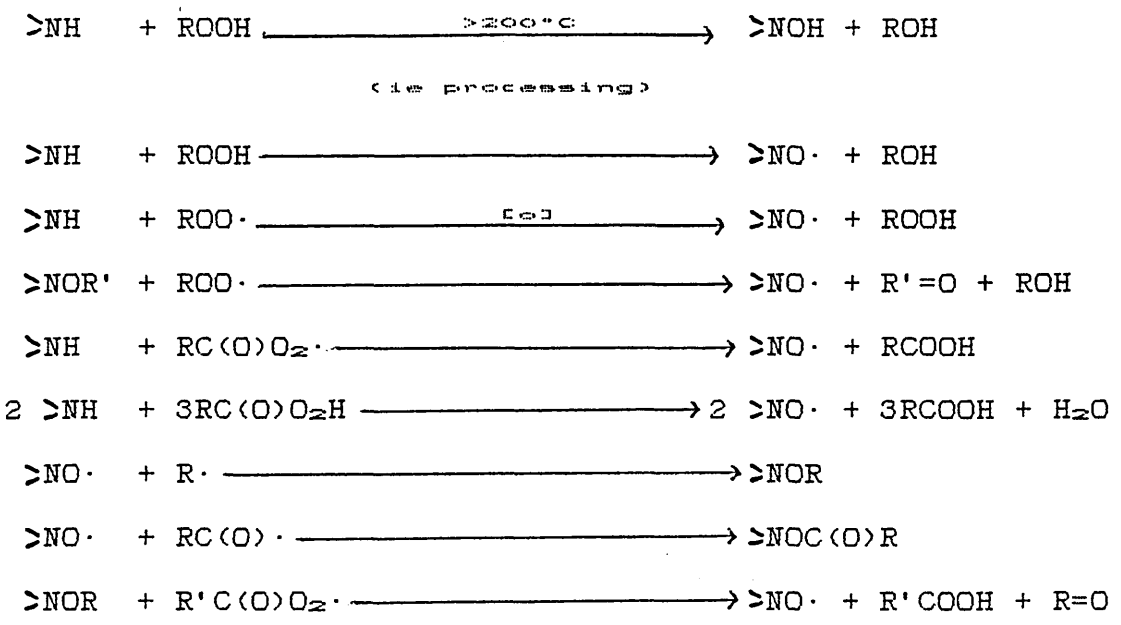
1.5. HINDERED AMINE LIGHT STABILIZERS: THEIR MODE OF ACTION AND TRANSFORMATION PRODUCTS

In addition to the effects of thermal processing polyolefins also suffer degradation on exposure to light. In order to facilitate their long term use in situations where there is exposure to light, and in particular for outdoor applications, light stabilizers are added during their manufacture. Hindered amine light stabilizers (HALS)

have been found to be particularly effective in fulfilling this role. These compounds are based on 2,2,6,6-tetramethyl-piperidine and have been available commercially for about the last twenty years.

Over this time they have been the subject of a considerable amount of research, particularly concerning their mechanism of action, which has been the cause of some controversy.[57] Their primary mode of functioning appears to be the trapping of carbon-centred radicals by nitroxyls and the regeneration of nitroxyls from the N-alkyloxy products of alkyl radical trapping. Tetramethylpiperidines and their nitroxyls can also form complexes with hydroperoxides and this improves their performance.[58] Their mechanism of action has been discussed in great detail by Gugumus, including the intermediates formed.[59] A few of the important reactions are given in scheme 2.[58]

SCHEME 2 - Reactions relevant to the photostabilization of polyolefins by HALS.



Many different HALS have been synthesised but, as with antioxidants, those which are monomeric and of lower molecular weight are of higher volatility and therefore more likely to be lost during processing and end use.[33] To overcome this, higher molecular weight and polymeric HALS have been developed. Tinuvin 622 is one such polymeric HALS and it was used during this study.

Although there has been a large amount of literature concerning the mechanism of HALS action there is little, if any, relating to the effects of ionizing radiation upon HALS in polyolefins.

HALS are excellent photostabilizers but do not fulfil the requirements expected of processing stabilizers. They are therefore often used in combination with hindered phenolic antioxidants which opens up the possibility of interactions between the two types of stabilizer and their respective transformation products. These interactions have been studied in some detail.[57,60,61,62] Allen draws a number of important conclusions regarding this.[61]

i) Hindered phenolic antioxidants antagonise the photostabilizing action of HALS.

ii) Hindered phenolic antioxidants and HALS synergise during thermal oxidation.

iii) Antagonism is associated with the prevention of the formation and removal of nitroxyl radicals from the cyclic regenerative mechanism by antioxidants and their transformation products.

iv) Synergism is associated with the complementary behaviour of nitroxyl radicals with phenolic antioxidants.

v) The effects are dependent upon additive concentrations, manufacturing history and the presence of other additives such as pigments.

1.6 PREVIOUS RESEARCH AT SHEFFIELD CITY POLYTECHNIC

Throughout the last nine years there have been three research projects investigating the effects of irradiation upon additives in various polymers. The first of these examined the effect of irradiation on organotin stabilizers in PVC.[63] The second involved the investigation of the effects of gamma irradiation on additives in food-contact polymers.[64] Finally, the present study has involved the investigation of the effects of electron-beam irradiation on additives in food-contact polymers and builds on and complements the work carried out in the previous study. It is therefore necessary to review the aims and conclusions of the previous study.

1.6.1 AIMS AND CONCLUSIONS OF THE PREVIOUS STUDY

The aims of this study were to investigate the effect of various doses of gamma irradiation on :

i) the extractable levels of several hindered phenol antioxidants in polymers.

ii) the extent of migration of antioxidants from polymers into food simulants

and to:

iii) detect, separate and identify any antioxidant transformation products produced as a result of gamma irradiation.

iv) to determine whether or not antioxidant fragments become polymer bound upon gamma irradiation and, if so, the extent to which this occurs.

The main conclusions of the investigation were as follows :

i) A dose related reduction in the level of extractable antioxidant occurs upon exposure of the polymers to gamma irradiation.

ii) A dose related reduction in the amount of antioxidant migrating from polymers into fatty food simulants occurs upon exposure of the polymer to gamma irradiation.

iii) 2,6-Di-t-butyl-1,4-benzoquinone was identified as an extractable transformation product of phenolic antioxidants.

iv) 3,5,3',5'-tetra-t-butylstilbene-4,4'-quinone (I) was identified as a transformation product of the antioxidant Irganox 1330.

v) There is a dose-related increase in the level of antioxidant transformation products binding to the polymer.

vi) The antioxidant Irgafos 168 was found to be transformed to its related phosphate upon gamma irradiation.

1.6.2 THE PURPOSE OF THE PRESENT STUDY

One of the main advantages of irradiation as a food processing method is the unique possibility of treating foods, after they have been packaged.[4,5] This, of course, involves irradiating the packaging material too, which usually contains stabilizers. Although the effect of irradiation on the physical properties of stabilized polymers has been examined [65,66], there have been few studies concerning the effect of irradiation on the stabilizers in the polymers. Jaworska has studied this but using doses of irradiation well above those used to irradiate food and without reference to any stabilizer transformation products produced.[67] Kiss *et al* suggested that the effects of irradiation and thermal aging are different; but they too failed to address the problem of transformation products.[66] Shanina *et al* and Gugumus examined the effects of thermal treatment upon antioxidants in polypropylene and suggested the types of

transformation products which may be present but not their exact structures.[68,69] Since there is increasing concern about the effects of irradiation upon the packaging polymers and a wider awareness of such issues [19,20,70], this type of study is important. There is also a great deal of concern about the possible migration of additives and any irradiation-produced transformation products from the packaging into foods.[19,71,72] The EC is also concerned with this subject from a legislative point of view.[73]

The previous project concerned the effects of gamma irradiation on antioxidants in food-contact polymers. However, it was possible that electron-beam irradiation would produce different effects since the dose rates possible are much greater.[9] Thus the time for oxygen diffusion into the polymer is more limited than in gamma irradiation.

Azuma *et al* reported that irradiating polyethylene using an electron-beam rather than a gamma irradiator reduced the amount of volatiles produced.[74] Therefore it was deemed necessary to investigate the effects of electron-beam irradiation on additives in food-contact polymers to complement the earlier work. The work carried out during the research programme can be divided into two parts. Firstly, the investigation of the effects of electron-beam irradiation on the levels of additives present in polyolefins has been investigated along with the levels of migration of antioxidants from irradiated polyolefins into a fatty food simulant. This work is detailed in chapter 3.

The second phase has involved the identification of antioxidant transformation products discovered during the first phase of the project. This work is detailed in chapter 4.

1.6.3 AIMS OF THE RESEARCH PROGRAMME

The aims of this research programme were as follows :-

1. To investigate the effect of electron-beam irradiation on antioxidants present in food-contact polymers.
2. To compare the effects of gamma and electron-beam irradiation on antioxidants in polyolefins.
3. To investigate the effects of irradiation on additive/polymer combinations not previously investigated.
4. To investigate the effects of electron-beam irradiation on the migration of antioxidants from polymers into a food simulant and compare these results with those previously obtained for gamma irradiation.
5. To detect, separate, identify and quantify any extractable antioxidant transformation products produced by irradiation.

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2.1 FORMULATION OF SAMPLES

The polymer samples used for the investigations carried out during the present study were provided by ICI (Chemicals and Polymers Group) PLC and BP Chemicals (London).

The polypropylene homopolymer beads provided by ICI had been prepared in the following way. Samples of unstabilized polypropylene homopolymer powder were intimately mixed with each of five additives at concentrations of 0.1, 0.2, or 0.25% by weight. The additives used were Irganox 1010, Irganox 1076, Irganox 1330, Irgafos 168 and Tinuvin 622. Small pellets of stabilized polymer were then prepared from these mixtures using conventional hot milling or sintering. Two polypropylene copolymer samples were also provided by ICI. The copolymer contained 5% polyethylene by weight. The samples were prepared by intimately mixing two batches of unstabilized polypropylene copolymer powder with either Irganox 1010 or Irganox 1076, both at a concentration of 0.25% by weight. After mixing, small pellets of stabilized polymer were then prepared using conventional hot milling or sintering. In order to facilitate the migration testing, thin sheets of both homopolymer and copolymer types of polypropylene containing either Irganox 1010 or Irganox 1076 at an initial concentration of 0.25% by weight were prepared by hot milling followed by

compression moulding techniques. BP also provided three stabilized polymers, an LDPE sample containing Irganox 1076 at a concentration of 0.2% by weight and two lLDPE samples. The two lLDPE samples both contained 0.15% Calcium Stearate by weight and 0.10% Stearamide by weight; however one of these also contained 1.0% by weight of Irganox 1076 and the other 0.1% by weight of Irganox 1076. Small pellets of these samples produced by sintering were provided.

2.2 IRRADIATION PROCEDURES

Irradiation by both gamma rays and electron-beam was carried out in air. For gamma irradiation, polymer samples (usually about 20g) were placed in glass vials, which were then wrapped in tissue paper, to prevent breakages, and boxed. The samples were irradiated by Isotron PLC using a cobalt-60 source at a dose rate of 12.5kGy per hour. Different batches of samples were exposed for varying lengths of time resulting in a range of doses of irradiation, the usual doses being 1, 5, 10, 25 and 50 kGy. For electron-beam irradiation, polymer samples (usually about 20g) were placed in thin paper envelopes. The samples were irradiated by Viritech Limited (a firm which now forms part of Isotron PLC) using a 4.5 MeV Dynamitron continuous d.c. electron-beam facility. Different batches of samples were exposed for various times resulting in a variety of different doses of irradiation, the usual doses being 1, 5, 10, 25 and 50kGy.

After irradiation, all the samples were stored in the dark.

2.3 EXTRACTION PROCEDURES USED FOR ANTIOXIDANTS AND THEIR TRANSFORMATION PRODUCTS

In order to analyse the antioxidants and their transformation products contained in polymer samples, by chromatographic methods, it is necessary to extract them from the polymer.

Various extraction methods have been used by different workers. Most recently, antioxidants have been extracted from polymers by heating in a sealed vessel in 1,1,1-trichloroethane or an acetone/n-heptane mixture, using microwaves. Using this method 90-100% of the antioxidant was extracted in three minutes.[1] Supercritical fluid extraction using carbon dioxide is also becoming more popular.[2-4] This method is also quick and can be carried out at relatively low temperatures; however it requires more complicated apparatus than other methods. Soxhlet extraction has been a popular method in the determination of antioxidants, using various organic solvents to extract the antioxidants, such as trichloromethane [5,6] or dichloromethane [5,7,8] for lengths of time varying from 3 to 48 hours. Certain polymers can also be dissolved by solvents such as decalin [9,10] and xylene [11], thereby freeing the antioxidant from the polymer which can then be reprecipitated and discarded. Antioxidants have been extracted from polymers using organic solvents at room

temperature [12]; however this process requires a long exposure time. By far the simplest and almost the quickest method which has been used is to heat the polymer under reflux in an organic solvent. Various solvents have been used including THF [13,14], tetrachloromethane [13], trichloromethane [7,15] and hexane.[14] The exposure time used has varied from 0.5 - 6 hours. If necessary, oligomers can be removed from the resulting extract by precipitation with a solvent such as acetone.[13,16]

This type of procedure was chosen for this present study. Smith has described experiments carried out in order to determine the reflux time required.[17] A reflux time of four hours was found to remove about 91% of the antioxidant in an unirradiated sample of similar composition to that used in the present study. Five hours removed an additional 4% of the antioxidant claimed to be present by the manufacturer, but longer times than this extracted no further antioxidant.

In order to avoid the process taking an inordinate amount of time, a reflux time of 4.5 hours was chosen for the present study. Since the results are obtained on a comparative basis, this was deemed to be more than adequate. Reproducibility tests had also been undertaken during the previous investigation [17], the results proving satisfactory.

The procedure used during the present study to extract any of four antioxidants present in polypropylene, low density polyethylene or linear low density polyethylene, after varying doses of electron-beam or gamma irradiation, is

given below. The four antioxidants in question are Irganox 1010, Irganox 1076, Irganox 1330, and Irgafos 168. Stabilized polymer beads (0.5g) were weighed accurately and placed in a 25ml round-bottomed flask along with trichloromethane or 1,1,1-trichloroethane (10ml). For the quantitative analyses, the solvent was then spiked with internal standard solution.

Irganox 1010 was used as the internal standard for Irganox 1076 and *vice versa*. Irganox 1010 was also used as the internal standard in the determination of Irgafos 168 while Irganox 1076 was used during the determination of Irganox 1330. The mixture was then heated under reflux for 4.5 hours. After heating under reflux, the trichloromethane or 1,1,1-trichloroethane extract was removed from the polymer and microfiltered, as described below. The polymer beads were washed with trichloromethane or 1,1,1-trichloroethane and the washings were also microfiltered and added to the previous filtrate.

The microfiltration was carried out using a Hamilton 5.0ml gas-tight syringe #1005 with a Micro Filtration Systems model number kS-13 stainless steel microfiltration unit attached containing Whatman 1.0cm GF/D glass microfibre prefilters and Rainin Instrument Co. Inc. 13mm diameter 0.45µm pore size nylon-66 membrane filters. The solution was drawn into the Hamilton syringe through a Teflon® needle. The extracts were kept in amber borosilicate glass screw cap septum vials fitted with Tuf-bond™ Teflon®/silicone discs to prevent evaporation. The trichloromethane or 1,1,1-trichloroethane was removed by

careful evaporation under oxygen-free nitrogen. Ethyl acetate (3ml) was added to precipitate out more polymer fragments and the solution was re-microfiltered. The solvent was then removed by evaporation under oxygen-free nitrogen and ethyl acetate (0.5ml) was added. The solvent used to redissolve the extract can be important since halogenated solvents can cause peak fronting during chromatographic analyses such as those used during this study.[18] This can be avoided by using acetone, acetonitrile, ethyl acetate, methanol or THF. In this study ethyl acetate was chosen because of its compatibility with the hplc mobile phase.

As well as extracts from the polymer samples which had received irradiation doses of 0,1,5,10,25 and 50 kGy, spiked extracts of unstabilized polymer beads prepared as standards for calibration were analysed. The calibration standards were prepared in the following way:-

Unstabilized, unirradiated, polymer beads were placed in a 25ml round-bottomed flask along with trichloromethane (10ml). The mixture was then spiked with a known amount of the analyte antioxidant commensurate with its concentration in the sample. The mixture was also spiked with the internal standard in the same manner as for the samples. Three different standards of different analyte concentration were prepared together with a blank containing unstabilized polymer but no analyte antioxidant. The standards were treated in exactly the same way as the actual samples. All the extracts were kept in the dark prior to analysis.

It was possible that, during the reflux procedure, some of the internal standard antioxidant spike may have been absorbed by the polymer and become physically trapped within it, while remaining in equilibrium with the antioxidant in trichloromethane solution. This would give artificially high results for the percentage of analyte antioxidant remaining. Therefore a simple experiment was carried out to investigate this point.

Unstabilized, non-irradiated polypropylene (0.5g) was placed in a 25ml round-bottomed flask along with trichloromethane (10ml). This mixture was then spiked with a solution containing 1.25mg of Irganox 1076 in trichloromethane. The contents were heated under reflux for 4.5 hours after which time the polymer beads were removed and the extract was microfiltered before being chromatographed as detailed in section 2.8.

The polymer beads were then placed in another 25ml round-bottomed flask along with fresh trichloromethane (10ml) and heated under reflux for a second time, for a further 4.5 hours. The polymer beads were then removed and the extract was microfiltered and chromatographed, as detailed in section 2.8. A blank experiment was carried out in a similar way but omitting the polymer.

The chromatogram for the first extract showed one peak with a peak height equivalent to that of the blank which was identified as the Irganox 1076 peak. No peaks were visible in the chromatogram for the second extract. The chromatograms were run at the same attenuation settings. These experiments indicate that a negligible amount of the

spike is physically trapped within the polymer. Thus the use of the internal standard method was vindicated.

2.4 ANALYTICAL METHODS USED TO DETERMINE HINDERED PHENOL ANTIOXIDANTS

The analysis of polymer additives has always been a challenge for analytical chemists due to the wide variety of additives available, the low volatility of many of them, and the fact that often quite complex mixtures of additives are used to stabilize polymers.[18,19] The antioxidants Irganox 1010, Irganox 1076, Irganox 1330, and Irgafos 168 have been separated and analysed by various chromatographic methods. Thin Layer Chromatography (TLC) has been used qualitatively [20,22] but is difficult to use quantitatively. Size Exclusion Chromatography (SEC) has been used in conjunction with a UV detector [23] or a refractive index detector [23,24] for 1010, 1076 and 1330 and linked in series with GC-MS for 1076 and 1330.[24] However it often gives poor resolution and lacks the sensitivity of some other methods.

Gas Chromatography (GC) with a Flame Ionization Detector (FID) has been used for 1076, 1330 and 168.[11,15,25-27] However, in the case of 1010, very high temperature capillary GC is required, 1010 only eluting at a temperature of 395°C.[25] Denning and Marshall [27] report using a lower temperature of 250°C; however it seems more likely that this peak was due to a decomposition product. Transesterification of 1010 and 1076 has also been carried

out followed by Gas Chromatography with Mass Spectrometry used as the detection method (GC-MS).[28,29]

Because of the low volatility of many antioxidants, the preferred method of analysis has traditionally been High Performance Liquid Chromatography (HPLC).[2,19] Normal phase hplc (NP-HPLC) has been used with UV detection for all four of the antioxidants by various workers [6,9,10,14,24,30,31] and also with a refractive index detector for 1010 and 1330 [24], although refractive index detection is not a very sensitive or specific method. However, the preferred mode of hplc for these compounds is reversed phase (RP-HPLC), since this gives the most reproducible results.[18,26] RP-HPLC using UV detection has been used for all four antioxidants by various workers [1,2,7,13,16,26,32,33] and for 1010, 1076 and 1330 using a refractive index detector.[7] The most versatile form of UV detector which has been used is the multichannel detector which allows the UV spectra of compounds to be recorded as they elute from the column. [18,34] RP-HPLC has also been used successfully with a mass spectrometer as the detector. However, these two techniques are difficult to interface. Only one group of workers appears to have successfully accomplished this, by using a moving belt interface.[12,35]

The most recent technique to be applied to the analysis of polymer additives is Supercritical Fluid Chromatography (SFC). This technique combines some of the advantages of both GC and LC and has been used to detect all four antioxidants using two detection methods,

FID [3,5,8,30,32,36] and Fourier-transform infrared spectrophotometry (FT-IR).[4,19]

Although many workers have determined the levels of antioxidants in polymers, very few have made mention of the fact that in real polymer systems the antioxidants often undergo transformation processes. Francis *et al* note that additives can undergo thermal decomposition but they fail to deal with the analysis of the resulting compounds.[13] Lichtenthaler and Ranfelt carried out thermal aging of polyethylene samples stabilized by Irganox 1010 and Irganox 1076. Several transformation products were detected, however they made no attempt to identify them.[6]

Since SFC is not available, as yet, at Sheffield City Polytechnic, RP-HPLC seemed the obvious choice for routine analysis. The method chosen was based on a procedure used by Ciba-Geigy Limited, who manufacture the antioxidants, for the determination of Irganox 1010 and Irgafos 168. Their method involves reversed phase HPLC using a 30cm long C_{18} column at ambient temperature. The mobile phase consisted of ethyl acetate:methanol:water 52:38:10 v/v. A UV detector was used with a monitoring wavelength of 280nm. The analytical methods used to determine the antioxidants during the present study are detailed later in chapter 2.

2.5 ANALYTICAL METHODS USED TO DETERMINE TINUVIN 622

Tinuvin 622, being different in its chemical type and also polymeric, requires different types of analytical methods. Perlstein and Orme [37] have determined it using pyrolysis-GC with a packed column and flame ionization detection. Roberson and Patonay [38] also used pyrolysis-GC but with a capillary column and a nitrogen-phosphorus detector. Mika *et al* [39] determined HALS including Tinuvin 622 in polyolefins by performing a quantitative micro-analysis of nitrogen in the sample.

Whilst these methods are undoubtedly the most effective methods for determining Tinuvin 622 it was felt that irradiation of polypropylene containing Tinuvin 622 may produce UV absorbing species unlike Tinuvin 622 which could be extracted using the same method that was used for the antioxidants. Therefore polymers stabilized by Tinuvin 622 were extracted and analysed in the same way as polymers stabilized by phenolic antioxidants. The hplc method used is detailed in section 2.8.

2.6 GC METHOD

Gas chromatography was carried out using a Varian 6000 Gas Chromatograph connected to a Varian Vista 402 Data Station. The columns used were fused silica capillary columns with internal diameter 0.32mm either 25,5 or 1m long with an OV-1 bonded stationary phase 0.25μm thick. A temperature programme was used involving holding the column at 60°C for two minutes then increasing the

temperature to 300°C at 4°C per minute. The column was then held at 300°C for 30 minutes. The FID was set at 350°C and the injection port temperature was varied between 200 and 350°C. The carrier gas was nitrogen.

2.7 GC-MS METHOD

Gas chromatography - Mass Spectrometry was carried out using a Hewlett Packard 5890A Gas Chromatograph linked to a VG Trio-1 Quadrupole mass spectrometer in Electron Impact mode using the VG Lab-Base data system. The GC columns used were fused silica capillary columns with internal diameter 0.32mm either 25 or 5m long with an OV-1 bonded stationary phase 0.25μm thick. A temperature program was used involving holding the column at 60°C for two minutes then increasing the temperature to 300°C at 4°C per minute. The column was then held at 300°C for 30 minutes. The injection port temperature was 150°C.

The mass spectrometer ion source was set at 200°C and the electron energy at 70eV. The resulting mass spectra were compared by the computer with those contained in the NBS spectral library.

2.8 HPLC METHODS

1) Extracts used during the determination of the effects of electron-beam irradiation on the levels of antioxidants in polymers were chromatographed in the following way:-

The hplc system consisted of a Gilson model 302 pump, a Gilson model 802 manometric module and a Gilson HM Holochrome UV monitor set at 275nm. The columns used were supplied by Phase Separations Limited, the 5cm long guard column contained Spherisorb S10 ODS1 and the 10cm long analytical column contained Spherisorb S5 ODS1. The injection valve was a Rheodyne 7125 fitted with a 20µl loop. The loop was partially filled using an SGE 10µl 10A-RLC syringe. It is known that using an injection volume greater than 10µl of a solvent other than the mobile phase itself can cause distortion of the chromatographic peaks.[7] The chromatograms were recorded using a Houston Instruments Omniscribe recorder with the chart speed set at 1cm min^{-1}. The mobile phase used contained ethyl acetate, methanol and water, 50:40:22 v/v respectively. The ethyl acetate and methanol were hplc grade solvents supplied by FSA and the water was distilled. The mobile phase was degassed using a Kerry KS-100 ultrasonic bath before use.

2) Extracts used to identify and analyse the antioxidant transformation products were chromatographed using a hplc system consisting of a Philips PU 4015 pump linked to a Philips PU 4021 multichannel UV detector (incorporating a linear diode array). The detector was controlled and the data processed using a Dell 210 microcomputer fitted with the Philips PU 6003 Diode Array Detector system (V.3.0) software and linked to an Epson LX-850 printer. The columns, valve, syringe and mobile phase used were the same as those listed above. When required, fraction

collection of the hplc effluent was achieved using a Gilson F203 Microfraction collector operating in peak mode.

3) The gradient hplc analyses were carried out on a system consisting of two Gilson model 305 piston pumps and a Gilson model 805 manometric module linked to a Gilson model 811B Dynamic Mixer of internal volume 1.5ml. The samples were injected using a Gilson 401 Diluter and 231 Sample Injector via a Rheodyne 7010 injection port fitted with a 100µl sample loop. The usual sample size was 10µl. A small particulate matter pre-filter was placed before the Hichrom ODS1 S5 25cm long analytical column. Detection at 275nm was achieved using a Severn Analytical SA6504 programmable absorbance detector and the results were recorded using a Kipp and Zonen BD41 chart recorder with the chart speed set at 1cm min^{-1}.

The mobile phase involved the use of two mixtures, the first (A) consisted of methanol:water 10:90 v/v, respectively and the second (B) of ethyl acetate:methanol 50:38 v/v, respectively. The mobile phase composition was held at 65% B for four minutes after which time the proportion of B was increased to 90% over a period of twenty minutes. This composition was held for ten minutes after which time the proportion of B was increased to 100% for a further five minutes. The flow rate was kept constant at 1ml min^{-1}. The mobile phase was degassed by bubbling helium through it before use.

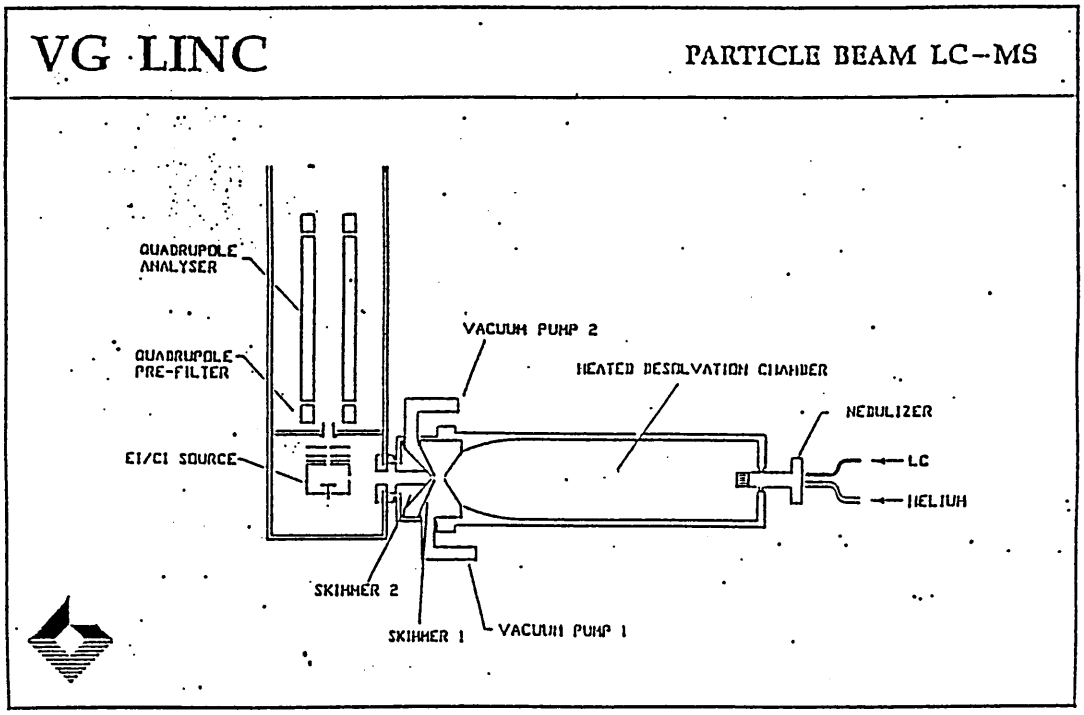
2.9 HPLC-MS METHOD

HPLC can be interfaced with mass spectrometry in a variety of ways. However, experience has shown that these interfaces are either difficult to set up and operate as with moving belt interfaces or they do not generate spectra that can be searched against mass spectral libraries, as in the case, for example, with thermospray and Plasmaspray interfaces.[40]

VG Masslab Limited has recently developed a new technique to achieve this, the VG Linc™ particle-beam interface. This interface provides a simple means of obtaining reliable, reproducible EI, positive CI and negative CI mass spectra on a routine basis. The EI spectra can be library-searched using the NBS library. A wide range of HPLC solvents may be used with a flow rate in the range 0.1 to 1.0ml min^{-1}. No adjustment to the working mobile phase is required. The other interfaces are not able to operate in this way. A diagram of the interface is contained in figure 2.1. The mobile phase is nebulized using Helium gas and drawn through the heated desolvation chamber under vacuum. The solvent is removed from the products carried by the mobile phase and they are then drawn through dual momentum separator skimmer plates and into the mass spectrometer ion source as a narrow beam of particles.

FIGURE 2.1

- A schematic diagram of the VG Masslab Linc™ particle-beam interface.



The particle beam interface used during this study was a prototype provided by VG Masslab Ltd. The helium flow could not be measured exactly on this prototype, however the back pressure was about 16psi. Also it was not possible to control the desolvation chamber temperature or measure it accurately; however, it was about 60°C.

Hplc conditions were the same as those described in section 2.8 1) except that a flow rate of 0.7ml min^{-1} was used. A VG Trio-1 Quadrupole mass spectrometer was used in electron impact mode along with the VG Lab-Base data system. The source temperature was set at 200°C and the electron energy at 70eV. The mass range used was 60-950 mass units.

2.10 METHOD USED FOR MIGRATION TESTING

"Migration" is a convenient term widely used to describe the loss of additives from polymers. Practically no plastic material is completely resistant to persistent chemical or physical attack by foodstuffs. Hence the contamination of food by small amounts of a large variety of complex chemicals, including antioxidants, is inevitable.[41] Obviously, it is essential to be aware of this process and the extent to which it occurs, in order to maintain public safety. Migration is generally assumed to be a diffusion-controlled process and is thus dependent on the concentration of the additive in the polymer, the temperature, the density of the plastic, the contact time and the physio-chemical properties of the polymer, the

additives and the foodstuff.[42,43] However, Gandek [44] reports that except in the case of very large migrants diffusing at low temperatures, short-time migration is not controlled by diffusion in the polymer. The uncertainty regarding the actual mechanism of migration and the fact that it is dependent upon a wide variety of variables makes mathematical modelling difficult [44] and experimental measurement essential.

Foodstuffs are usually very complex chemical mixtures which makes the analysis of small amounts of migrants, which may be present in them, difficult or impossible. Therefore, various solvent-media have been used as food simulants to allow easier determination of the various migrants. For organic chemicals such as antioxidants and their transformation products, migration is at its greatest when the polymer is in contact with fatty foods since these compounds are more soluble in fatty foods than in aqueous phases.

The simulant which has traditionally been used for fatty foods is olive oil; however this still causes problems during analysis, such as poor reproducibility and accuracy [45,46], as also does HB307 (a slightly simpler mixture of triglycerides which has also found use).

To overcome these problems, various organic solvents have been suggested as simulants such as n-hexane, n-heptane, isooctane, ethoxyethane, ethanol and others.[41,42] These simpler simulants are very different in chemical structure from the foodstuffs themselves or even from olive oil and HB307. They also interact with plastics in different ways.

Therefore, they cannot be regarded as accurate simulants but only as useful indicator simulants of value for assessing trends in migration.[42,45,47]

The best of these indicator simulants is isooctane. The performance of isooctane as a simulant has been studied extensively by De Kruijf and Rijk.[46] They examined the overall migration from a total of 130 commercial packaging materials including homogeneous plastic films, laminates, polyethylene-coated board samples and food utensils into isooctane during two days at 20°C and into olive oil during 10 days at 40°C. The conclusion from this study was that for 95% of the samples the values obtained in the isooctane and the olive oil tests were consistent. Although for the specific migration of some antioxidants from various polymers, significant differences were observed between the values obtained with isooctane at 40°C over a period of two hours and those obtained with olive oil at 40°C over a period of ten days. Hence, using the lower temperature of 20°C and a contact time of two days is advisable for isooctane.

The methodology and theory of migration is discussed in detail elsewhere [42] as are the legislative controls to be enforced by the European Community.[48,49]

Since it is likely that some food products will be irradiated after they have been packaged, it is important to know what effect irradiation has on the levels of migration of antioxidants and their transformation products from food-contact polymers into foods.[42,50,51]

There has been little research into the effects of irradiation on the migration of additives from polymers.[50]

Figge and Freytag [52] report that the amount of the antioxidants BHT and Irganox 1076 migrating from polymers including polypropylene and polyethylene into HB307 after 10 days at 40°C is in the range 10-50% and that subjecting the polymer to a gamma irradiation dose of 25kGy reduced this to 8-38%. Lox *et al* [53] examined the total migration from PVC subjected to doses of electron-beam and gamma irradiation of between 3 and 25 kGy into water. They concluded that gamma irradiation increases migration at doses up to 10kGy but diminishes it above this dose. They also state that electron-beam irradiation has a different effect, producing a continuous dose related increase in migration which was consistently lower than that produced by gamma irradiation. This underlines the necessity for the present comparison between the effects of both types of irradiation on the migration of antioxidants from polyolefins. The method used for migration testing during the present study was based on that used by De Kruijf and Rijk [46] and is detailed below.

Polypropylene homopolymer or copolymer samples in sheet form containing 0.25% Irganox 1076 or Irganox 1010 were subjected to electron-beam irradiation doses of 1,5,10,25 and 50kGy. For each irradiated sample and the unirradiated samples, two strips of polymer of dimensions 40 x 17 x 1.6mm and one strip of dimensions 23 x 17 x 1.6mm were cut. Thus, the total surface area of polymer used was

40cm² per sample (35cm² for the main faces plus 5cm² for the edges). The accepted standard for migration measurements is 2dm² of polymer in contact with 100ml of simulant.[54] Therefore in this case 20ml of isooctane was used. The polymer was placed in a 25ml amber borosilicate glass screw-top vial sealed with a Tufbond™ Teflon®/silicone disc. The samples were left for two days at 20°C, after which time the polymer strips were removed and isooctane solutions were each spiked with internal standard solution. The internal standard consisted of Irganox 1076 or Irganox 1010 as appropriate dissolved in ethyl acetate, 100µl of the standard was injected into each isooctane sample. The samples were then carefully evaporated down to approximately 4ml using oxygen-free nitrogen, microfiltered in the usual way and further evaporated down to 0.1ml in 3ml Reacti-Vials™ sealed by Tufbond™ Teflon®/silicone discs. The resulting solutions were made up to 1.0ml using HPLC grade ethyl acetate. A control experiment was also carried out in the same way but without any polymer sample being present.

Six standard solutions of either Irganox 1076 or Irganox 1010 in ethyl acetate (10ml) along with the appropriate internal standard were made up.

The seven samples and six standards were then analysed using the usual hplc procedure detailed in section 2.8.

2.11 RADIOCHEMICAL STUDY OF THE EFFECTS OF ELECTRON-BEAM IRRADIATION ON IRGANOX 1076 IN POLYPROPYLENE AND HDPE

It has been shown that antioxidants or fragments of antioxidants can become covalently bound to polymers via radical coupling processes. This kind of process has been shown to occur in the case of BHT by Kovárová-Lerchova *et al* [56] and in the case of Irganox 1330 by Koch.[56] If the antioxidant or its fragments do become polymer bound they will be unable to migrate from the polymer into any food with which it may be in contact. Thus the public safety concerns about migration would be reduced.

In the previous study carried out at Sheffield City Polytechnic [17], Smith, investigated this possibility for Irganox 1076 using a radiochemical analysis. Smith also investigated the effect of gamma irradiation on this process. The general conclusions of this investigation were :-

i) that some polymer binding of Irganox 1076, or fragments derived from it, to polypropylene or HDPE does occur.

ii) that subjecting the polymer to gamma irradition increases the extent of binding in a dose related manner.

It was decided to carry out similar work to this using electron-beam irradiation in order to compare the effects of the two forms of irradiation on the binding of the antioxidant to the polymer. The work was carried out according to the method detailed below.

Radiolabelled Irganox 1076, [n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)-[3-^{14}C] propionate] was

synthesised, according to a method provided by Ciba Geigy Ltd., Basle, Switzerland, by the NATEC Institute. Details of the characterisation of this compound are recorded by Smith.[17]

Samples of this antioxidant were used to stabilize Polypropylene Propathene LYM42 provided by ICI and HDPE Lupolen 5261Z provided by BASF. This resulted in the formation of polypropylene, stabilized by 0.20% by weight of ^{14}C-Irganox 1076, of specific radioactivity 133 ± 7 kBq/g and in the formation of HDPE, stabilized by 0.19% by weight of ^{14}C-Irganox 1076 of specific radioactivity 123 ± 7 kBq/g. Details of the processing techniques used by the NATEC Institute are given by Smith.[17] The samples were provided in sheet form and kept in the dark wrapped in aluminium foil. Samples of the two polymers were subjected to electron-beam irradiation doses of 1,5,10,25 and 50kGy by Viritech Ltd. They were irradiated wrapped in a single layer of aluminium foil. These samples were analysed along with an unirradiated sample of each type of stabilized polymer.

Four strips of polymer of dimensions 1.8 x 0.9 x 0.09cm approximately were cut from each of the six samples for the two polymer types. The accurate mass of the four strips (ca 0.5g) was recorded. The four strips were then placed in a round-bottomed flask along with trichloromethane (4ml) and the mixture was heated under reflux for exactly four hours. The samples for all six doses were heated under reflux in parallel, simultaneously. After this time the trichloromethane

extracts were carefully removed in a quantitative manner using Pasteur pipettes and placed in separate 10ml volumetric flasks. A further 1ml of trichloromethane was added to each flask as a washing aliquot and then transferred to the appropriate volumetric flask in a similar manner. This extraction procedure was repeated to extract the samples exhaustively. The resulting trichloromethane solutions were made up to 10ml and mixed throroughly. Aliquots (3ml) of each solution were transferred to scintillation vials using bulb pipettes. The trichloromethane was removed from each sample by careful evaporation under oxygen-free nitrogen. Trichloromethane (1ml) and Cocktail O (2ml) were then added to each vial. The extractable radioactivity of the samples was measured using an LKB-Wallac Rackbeta model 1212 liquid scintillation counter in mode 2 for ^{14}C with a count time of 60 seconds. The samples were counted on the same day and a blank consisting of just trichloromethane (1ml) and Cocktail O (2ml) was included. The extractable counts per minute per gram of polymer were then calculated for each sample.

Although trichloromethane is known to quench the scintillation, since the same amount of trichloromethane is present in each sample, the effect can be ignored. Scintran Cocktail O is a mixture of 2,5-diphenyloxazole (PPO) (6g/l) and 1,4-di-2-(5-phenyloxazoyl) benzene (POPOP) (0.2g/l) in toluene and was supplied as a scintillation cocktail by BDH. The levels of radioactivity in the polymer strips before and after extraction were

determined. Measuring the radioactivity before extraction determines whether irradiation results in the production of volatile ^{14}C containing compounds, although this is unlikely. This would be indicated by a dose related reduction in radioactivity present before extraction. Measuring the radioactivity after extraction gives an indication of the amount of ^{14}C containing species becoming covalently bound to the polymer.

The radioactivity was measured using a Müller ZP1470 Geiger-Müller tube with a mica window of superficial density 1.5-2.5mg/cm^2 and a diameter of 24.1mm. The tube was held in an Ekco Electronics Ltd. shielded Geiger-Müller tube holder type N620, fitted into an Ekco Electronics Ltd. sample oven type N619A. The polymer strips were supported by a metal plate two at a time and held about 1cm away from, and exactly under, the Geiger-Müller tube, the same distance away for all the samples. The counts were recorded using a Thorn EMI Nuclear Enterprises Scaler Timer ST7 set on 600v. The preset time was set at 6 x 10^4s and the preset count at 400 for the extracted samples and 10,000 for the unextracted samples. The window setting was adjusted to 100 and the threshold to 20. All the samples were counted on the same day and the results were converted to counts per minute per gram. A correction for the background reading was also made.

2.12 THERMAL AGING METHOD

Polypropylene samples stabilized by antioxidants, in open Petri dish bottoms, were thermally aged in air at 150°C in a Gallenkamp Hotbox Oven with Fan (size 2). The samples were treated for a period of time which gave reductions in the levels of antioxidant similar to those caused by exposure to an irradiation dose of 50kGy. The samples were then stored in the dark.

Extractions and analyses were carried out according to the methods detailed earlier. This method is similar to that used by other workers.[57,58]

2.13 MODEL REACTIONS OF ANTIOXIDANTS WITH TERT-BUTYLPEROXYL RADICALS

tert-Butylperoxyl radicals can be used as models for the peroxide radicals produced in polymers during irradiation. They have been used by a number of other workers.[59-66] During the present study the four antioxidants used, Irganox 1010, Irganox 1076, Irganox 1330 and Irgafos 168 were allowed to react with t-butylperoxyl radicals generated from t-butylhydroperoxide using cobalt (II) acetyl acetonate as a catalyst. This was carried out in order to determine whether similar products are produced by this reaction to those produced during the irradiation of stabilized polymers. The method used is detailed below.

The required antioxidant (1 x 10^{-4} moles) was dissolved in trichloromethane (10ml) in a round-bottomed flask along with cobalt (II) acetyl acetonate catalyst (ca 180mg) and

an equimolar amount of t-butylhydroperoxide added (as a 70% aqueous solution). Ethanol (ca 2ml) was added to maintain miscibility. The mixtures were then heated under reflux for 4.5 hours after which time they were filtered and analysed by hplc using the usual method detailed in section 2.8.

2.14 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

^{1}H and ^{13}C nmr spectra were recorded using a Bruker WP 80SY spectrometer. ^{1}H chemical shifts were recorded on the δ scale, using tetramethylsilane as the external standard (δ=Oppm). The samples were dissolved in deuteriochloroform. ^{31}Pnmr spectra were recorded using a Bruker AM250 spectrometer. ^{31}P chemical shifts were recorded on the δ scale, using 85% orthophosphoric acid as the external standard. The samples were dissolved in deuteriochloroform. Shifts to high field are negative in sign.

2.15 DIRECT INSERTION PROBE MASS SPECTROMETRY

DIP-MS of solid samples was achieved using a VG Micromass Ltd. 7070F double focussing forward geometry mass spectrometer fitted with a heated probe. The probe was heated to about 400°C as quickly as possible. The source temperature was 200°C and the electron energy was set at 70eV. The mass range used was 200 - 1400 mass units.

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CHAPTER 3 - THE EFFECTS OF IRRADIATION ON THE LEVELS OF ADDITIVES IN POLYMERS

3.1 THE EFFECTS OF HEATING ANTIOXIDANTS UNDER REFLUX IN CONTACT WITH IRRADIATED UNSTABILIZED POLYPROPYLENE

It is known that transformation products of the antioxidant Irganox 565 are produced on heating it under reflux in trichloromethane with irradiated unstabilized polypropylene [1] presumably as a result of reactions with peroxo radicals produced upon irradiation of the polymer in air.[2] The chemical structure of Irganox 565 is shown in figure 3 1.

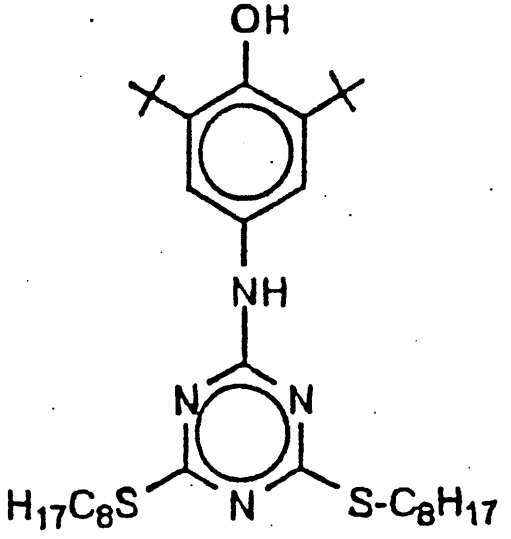

FIGURE 3.1 - CHEMICAL STRUCTURE OF IRGANOX 565

If the phenolic antioxidants used during this study are also susceptible to this process, the use of such antioxidants as internal standards could have been

rendered invalid. It was therefore necessary to investigate this phenomenon.

The method used was as follows:

A solution of the antioxidant in trichloromethane (200mg in 10ml) was prepared. Two aliquots (100µl) were removed from the volumetric flask. The first aliquot was heated under reflux in contact with non-irradiated, unstabilized polypropylene (0.5g) in trichloromethane (10ml) in a 25ml round-bottomed flask. The second aliquot was heated under reflux with 50kGy irradiated polypropylene (0.5g) in trichloromethane (10ml) in a 25ml round-bottomed flask. Both mixtures were heated under reflux for 4.5 hours. The trichloromethane solutions were then microfiltered in the usual way and carefully evaporated down to 1.0ml in 3ml Reacti-vials™ using oxygen free nitrogen. The extracts were chromatographed as detailed in section 2.8.

The attenuation settings were kept constant for each sample pair. Thus a measure of the effects of the irradiated polymer on the antioxidants was obtained by dividing the antioxidant peak height in the case of the irradiated polymer by the antioxidant peak height in the case of non-irradiated polymer.

The results of this determination are contained in table 3.1.

TABLE 3.1

TABLE SHOWING PEAK HEIGHT INDICES TO COMPARE THE EFFECT OF IRRADIATED, UNSTABILISED, POLYPROPYLENE ON VARIOUS ANTIOXIDANTS

ANTIOXIDANT	$\frac{\text{PEAK HEIGHT 50kGy}}{\text{PEAK HEIGHT 0kGy}}$
IRGAFOS 168	0.000
IRGANOX 565	0.005
IRGANOX 1330	0.069
IRGANOX 1010	0.379
IRGANOX 1076	0.494

Table 3.1 clearly shows that all the antioxidants are markedly affected by this process.

These results obviously have implications for the use of antioxidants as internal standards during the determination of the levels of extractable antioxidant from irradiated stabilized polymers. However, it should be noted that in the present study only Irganox 1076 and Irganox 1010 have been used as internal standards and these two antioxidants are the least affected of the five. Also, in the case of a routine determination of antioxidant levels in irradiated polymers, the polymers used are stabilized polymers which should markedly reduce the number of radicals present to react with the internal standard. Any reduction in the amount of internal standard relative to the analyte antioxidant would result in the calculated weight percentage of an antioxidant remaining being an over-estimate.

In order to determine the effect of this phenomenon on a routine determination, the analysis of Irganox 1076, 0.25% in polypropylene homopolymer, after irradiation doses of 1, 5, 10, 25 and 50kGy was carried out in the usual way using Irganox 1010 as the internal standard. By evaporating down to precisely 0.3ml in Reacti-vials™, the absolute peak heights of Irganox 1010 were accurately compared.

Within the experimental error of this analysis, no significant decomposition of the internal standard antioxidant, Irganox 1010, was found to occur. This result suggests that the use of Irganox 1010 and Irganox 1076 as

internal standards is acceptable, since Irganox 1076 is less affected than Irganox 1010. However, since the other antioxidants, which have not been used as internal standards, are affected by this process to a much larger extent, it would be prudent not to use them as internal standards for analyses involving irradiated polymers.

3.2 THE EFFECT OF ELECTRON-BEAM IRRADIATION ON THE LEVELS OF ANTIOXIDANTS IN POLYMERS

The results obtained to show the effects of a range of electron-beam irradiation doses on the extractable levels of various antioxidants from different polymers are presented in tables 3.2 - 3.5.

The results are given in terms of the percentage of initial antioxidant which remains extractable. The results of the effects of similar gamma irradiation doses, many of which were obtained during a previous study [1], are also included in the tables for comparison. Unless otherwise stated the polymer samples contained only the additive in question.

TABLE 3.2

COMPARISION OF ELECTRON-BEAM AND GAMMA IRRADIATION RESULTS

(% OF INITIAL ANTIOXIDANT PRESENT)

POLY-PROPYLENE SAMPLE	HOMOPOLYMER + 0.10 % IRGANOX 1010		HOMOPOLYMER + 0.10 % IRGANOX 1330		HOMOPOLYMER + 0.10 % IRGAFOS 168	
IRRADIATION TYPE / DOSE /kGy	ELECT-RON BEAM	GAMMA	ELECT-RON BEAM	GAMMA	ELECT-RON BEAM	GAMMA
0	100	100	100	100	100	100
1	75	88	93	87	38	52
5	52	63	69	66	<16	13
10	35	50	61	57	<16	6
25	19	25	38	39	<16	<6
50	11	13	24	29	<16	<6

In table 3.2 the amount of Irgafos 168 remaining after higher doses of irradiation is below the detection limit. This is indicated by the "<" sign followed by the limit of detection in percentage terms. The analysis of Irgafos 168 in polypropylene should ideally have been repeated with a preconcentration step introduced into the method, however time did not permit this to be undertaken.

TABLE 3.3

COMPARISION OF ELECTRON BEAM AND GAMMA IRRADIATION RESULTS

(% OF INITIAL ANTIOXIDANT PRESENT)

POLYPR-OPYLENE SAMPLE	HOMOPOLYMER + 0.25 % IRGANOX 1010		COPOLYMER + 0.25 % IRGANOX 1010		HOMOPOLYMER + 0.25 % IRGANOX 1076		COPOLYMER + 0.25 % IRGANOX 1076	
	TYPE OF IRRADIATION							
DOSE /kGy	ELEC TRON BEAM	GAMMA	ELEC TRON BEAM	GAMMA	ELEC TRON BEAM	GAMMA	ELEC TRON BEAM	GAMMA
0	100	100	100	100	100	100	100	100
1	107	NA	89	NA	85	NA	101	NA
5	72	NA	71	NA	79	NA	94	NA
10	59	48	70	53	68	74	86	86
25	35	29	40	28	53	60	76	63
50	22	11	38	11	44	57	58	55

NA = No analysis carried out

TABLE 3.4

COMPARISION OF ELECTRON-BEAM AND GAMMA IRRADIATION RESULTS

(% OF INITIAL ANTIOXIDANT PRESENT)

LOW DENSITY POLYETHYLENE SAMPLE	HOMOPOLYMER + 0.20 % IRGANOX 1076	
IRRADIATION TYPE / DOSE /kGy	ELECT -RON BEAM	GAMMA
0	100	100
1	97	100
5	88	88
10	79	81
25	59	58
50	32	35

TABLE 3.5

EFFECT OF IRRADIATION ON IRGANOX 1076 IN LINEAR LOW-DENSITY POLYETHYLENE (% OF INITIAL IRGANOX 1076 REMAINING)

LLDPE SAMPLE	LLDPE + 1.0% IRGANOX 1076 + 0.15% Ca STEARATE + 0.10% STEARAMIDE		LLDPE + 0.1% IRGANOX 1076 + 0.15% Ca STEARATE + 0.10% STEARAMIDE	
IRRADIATION TYPE / DOSE /kGy	ELECTRON -BEAM	GAMMA	ELECTRON -BEAM	GAMMA
0	100	100	100	100
1	100	95	90	85
5	95	92	58	74
10	91	91	84	57
25	79	78	43	19
50	72	67	23	6

The conclusions which can be drawn from these data are as follows :

i) Electron-beam irradiation causes a dose-related reduction in the level of extractable antioxidant.

ii) Electron-beam and gamma irradiation cause similar reductions in the levels of extractable antioxidant. This finding is in contrast to the findings of Azuma [3] who reports differences depending on the irradiation type in the production of volatiles from polyethylene. It would also suggest that enough oxygen is dissolved in the polymer prior to irradiation to allow oxidative degradation to take place. Thus the need for oxygen diffusion into the polymer, which is a slow process, during irradiation, is alleviated. Therefore, in effect, both irradiation processes are taking place with the same concentration oxygen available to promote oxidative degradation.

iii) Irradiation affects different antioxidants to different extents. This is clearly shown in table 3.2 where the results are shown for polypropylene homopolymer containing three different antioxidants, all at an initial concentration of 0.1% by weight.

Irgafos 168 is more susceptible to transformation than Irganox 1010 and Irganox 1330 is the least affected of this group of antioxidants.

In addition, table 3.3 shows that Irganox 1076 is less susceptible to transformation than is Irganox 1010.

iv) The extent of the reduction in extractable antioxidant is also dependent upon the initial concentration of the antioxidant. Table 3.5 highlights this for Irganox 1076 in lLDPE. Clearly there is a minimum amount of antioxidant needed to be present to protect the polymer from oxidative degradation during irradiation.

v) The type of polymer which the antioxidant is stabilizing also has an effect on the levels of extractable antioxidants after irradiation. This is confirmed by the data in table 3.3 which show that both Irganox 1076 and Irganox 1010 are slightly less affected when stabilizing the polypropylene copolymer (which contains only 5% polyethylene) than when stabilizing the polypropylene homopolymer. The initial concentration of Irganox 1076 is different in the LDPE and lLDPE samples from the polypropylene samples. However, it is possible to use the data contained in tables 3.3 - 3.5 to estimate that the extent of the decrease in antioxidant levels is in the order polypropylene homopolymer > polypropylene copolymer > LDPE > lLDPE. This appears to reflect the varying degrees of crystallinity within the polymers.

Radicals produced in the crystalline regions of polymers are only able to migrate to the amorphous

regions very slowly.[2] Thus at any given irradiation dose there will be less radicals available in a more crystalline polymer to react with the oxygen and antioxidant molecules which are concentrated in the amorphous regions.[2] Therefore, both oxidative degradation and the consumption of antioxidants will be reduced.

vi) The rate of decrease in extractable antioxidant remaining is greatest at the lower doses and moderates above 10kGy. This can be seen in figures 3.2 and 3.3 which represent graphically two sets of results, contained in table 3.2 to give a more visual presentation of the effects of irradiation on the levels of antioxidants in polymers.

This effect probably reflects the consumption of the limited amount of dissolved oxygen within the polymers. At low doses there is enough oxygen available for all the polymer radicals produced by irradiation to participate in oxidative degradation. This will result in greater antioxidant consumption. However, at higher doses the availability of oxygen is such that not all the radicals are able to participate in oxidative degradation and crosslinking starts to occur. Thus the rate of decrease in extractable antioxidant levels is greatest at the lower irradiation doses. Irradiation takes place too quickly for oxygen from the atmosphere to diffuse into the polymer and become involved in oxidative degradation.

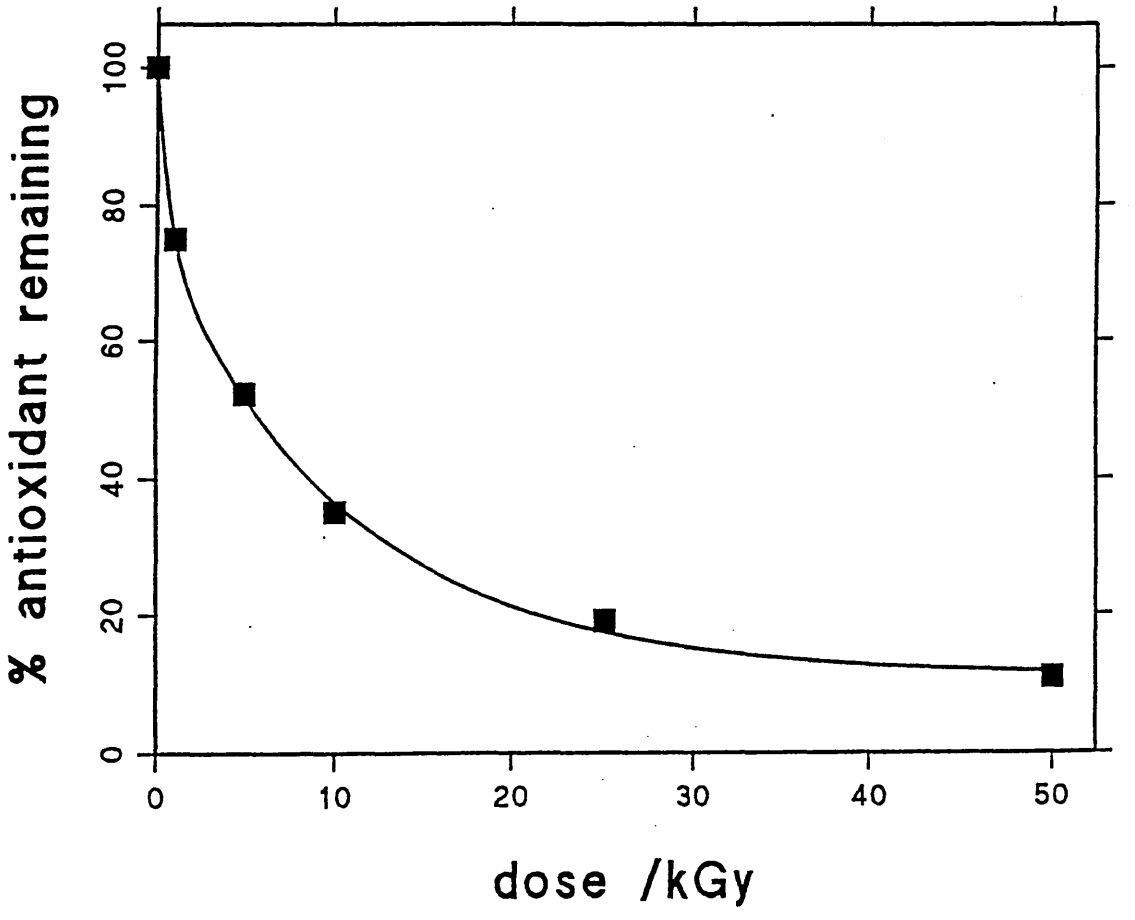

FIGURE 3.2 A graph showing the effects of increasing doses of electron-beam irradiation on the level of Irganox 1010 extractable from polypropylene homopolymer.

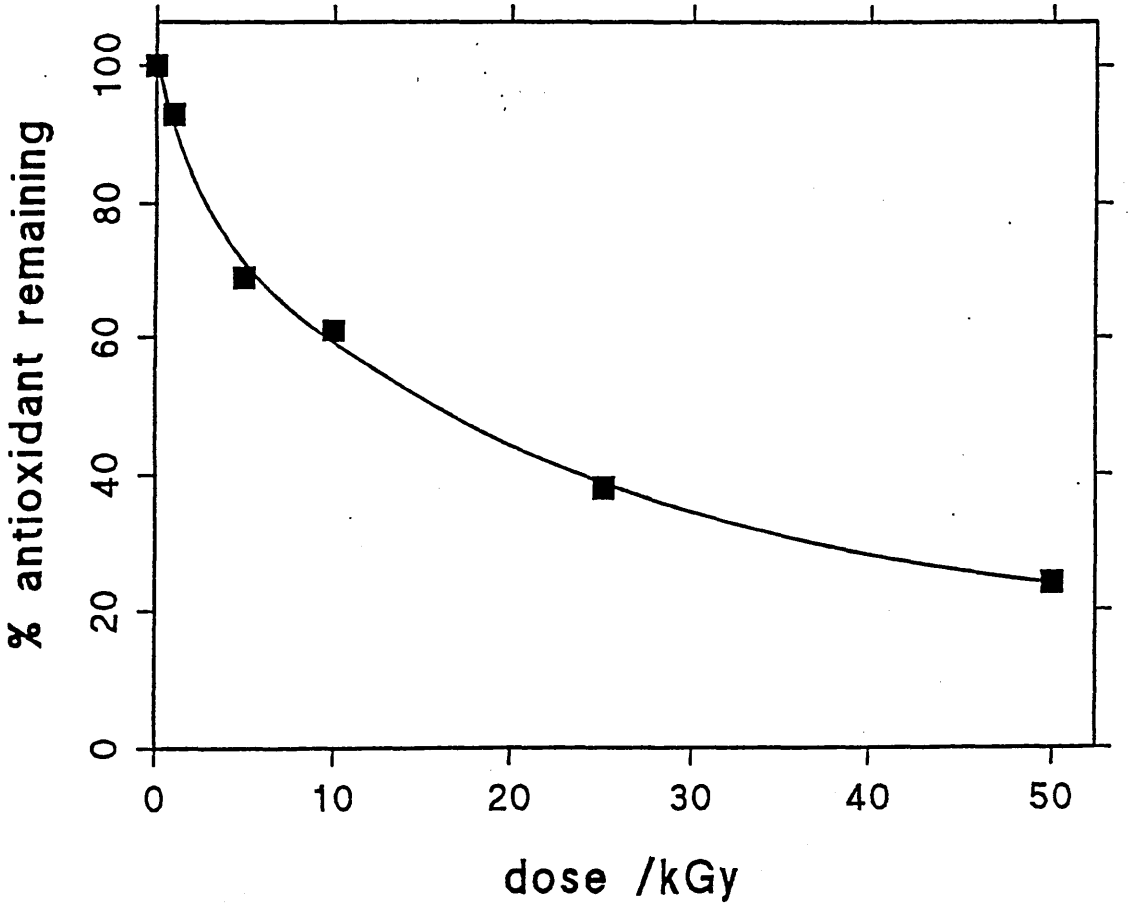

FIGURE 3.3 A graph showing the effects of increasing doses of electron-beam irradiation on the level of Irganox 1330 extractable from polypropylene homopolymer.

vii) Except in the case of Irgafos 168, enough antioxidant remains after an irradiation dose of 10kGy (the maximum dose permissible in food applications) to adequately stabilize the polymer. However, the fact that there is a significant decrease in the antioxidant levels up to 10kGy will obviously have to be taken into account by manufacturers supplying stabilized polymers for such applications. They may need to increase the initial level of antioxidant present.

viii) Obviously the reduction in antioxidant levels occuring upon irradiation must be accounted for in some way. During this work, many antioxidant transformation products were detected chromatographically under the same experimental conditions. The levels of transformation products were found to increase in a dose-related manner. This suggests that the antioxidants are converted to these transformation products upon irradiation of the polymer. Attempts to identify these transformation products are detailed in chapter 4 and some possible structures are proposed.

Literature references comparing the efficiencies of various antioxidants are sparse. Frank [4] suggests that Irganox 1076 is a more efficient processing stabilizer than Irganox 1010 but the order is reversed for oven aging polymers at 150°C. Gugumus [5], however, maintains that Irganox 1010 is more efficient in both cases.

Jaworska *et al* [6] studied the levels of extractable antioxidants in irradiated LDPE, but at doses of 0 - 600 kGy and the effects at lower doses, below 50kGy, are unclear. However, they do show that the amount of extractable antioxidant is decreased by irradiation which agrees with the findings presented here. They also agree with the results presented here in suggesting that Irganox 1010 is more affected by irradiation than Irganox 1076.

Thus the results above complement the published work providing additional details of the effects of irradiation on antioxidants in polymers.

The results were calculated using a Lotus-123® spreadsheet which was developed during the study. The spreadsheet presents the results for the levels of extractable antioxidant in polymers as weight percentages of antioxidant present and as percentages of the initial antioxidant present.
This spreadsheet used the data obtained for the standards to form a calibration line using linear regression analysis. Various statistical parameters were calculated to allow a check to be kept on the validity of the calibration.

The parameters calculated were as follows :

- the intercept of the regression line (a)
- the gradient of the regression line (b)
- the standard deviation of the intercept of the regression line (s_a)
- the standard deviation of the slope of the regression line (s_b)
- the 95% confidence interval for the intercept of the regression line
- the 95% confidence interval for the slope of the regression line
- the standard deviation of the y-residuals ($s_{y/x}$)
- the square of the product-momentum correlation coefficient (r^2)
- the limit of detection for the antioxidants

The linear regression line was then used to calculate the levels of antioxidants extracted from polymers. The 95% confidence intervals for each result were also calculated.

All the calculations were carried out using the formulae presented by Miller and Miller.[7]
For the sake of brevity only a selection of these results are presented here. Table 3.6 contains the statistical parameters for calibration data from three typical analyses.

TABLE 3.6

TYPICAL STATISTICAL RESULTS

STATISTICAL PARAMETER FOR REGRESSION LINE	DETERMINATION		
	IRGANOX 1330 0.1% in PP(H) 6 standards	IRGANOX 1010 0.25% in PP(C) 3 standards	IRGANOX 1076 0.20% in LDPE 5 standards
a	0.0236	- 0.0037	0.0009
b	36.16	3.91	3.23
s_a	0.0183	0.0169	0.0120
s_b	0.30	0.10	0.06
95% CI for a	+/- 0.0407	+/- 0.0401	+/- 0.0253
95% CI for b	+/- 0.67	+/- 0.23	+/- 0.13
$s_{y/x}$	0.0357	0.0243	0.0216
r^2	0.9993	0.9955	0.9940
LOD (wt%)	0.003	0.019	0.020

The data contained in table 3.6 allows the following conclusions to be drawn:-

a) in each case the origin falls within the 95% confidence intervals for the intercepts. This is important since the line would be expected to go through the origin.
b) the error for the slope is of an acceptable magnitude, the actual value being unimportant since it is dependent upon the amount of internal standard added.
c) the values for r, the product moment correlation coefficient, are all above 0.996. This gives an indication of how close the points are to lying on the calculated calibration line. A value of 1 would be perfect correlation.
d) the limits of detection are all well below the results for the amount of antioxidant extractable from the polymers subjected to an irradiation dose of 50kGy (see table 3.7).

The results for the levels of antioxidants remaining after various doses of electron-beam irradiation in samples of the same polymers are contained in table 3.7. Unlike tables 3.2 - 3.5 the results in table 3.7 are given in weight percentages and the confidence intervals, calculated using the spreadsheet, are also presented for each result.

TABLE 3.7

RESULTS FOR THREE TYPICAL ANALYSES PRESENTED

AS WEIGHT PERCENTAGES OF ANTIOXIDANT PRESENT

DOSE OF ELECTRON -BEAM IRRADIATION /kGy	DETERMINATION					
	IRGANOX 1330 0.1% in PP(H)		IRGANOX 1010 0.25% in PP(C)		IRGANOX 1076 0.20% in LDPE	
	wt% of 1330 present	95% CI |wt%|	wt% of 1010 present	95% CI |wt%|	wt% of 1076 present	95% CI |wt%|
0	0.085	0.0018	0.184	0.0100	0.256	0.0095
1	0.079	0.0018	0.164	0.0098	0.244	0.0093
5	0.059	0.0017	0.130	0.0099	0.226	0.0091
10	0.052	0.0017	0.128	0.0099	0.217	0.0090
25	0.033	0.0017	0.073	0.0108	0.142	0.0089
50	0.021	0.0018	0.069	0.0109	0.084	0.0095

If the confidence intervals for the results overlap, some doubt exists as to whether the two values are infact different. The magnitude of the overlap being a measure of the doubt which exists. In the case of the determination of 1330 in polypropylene homopolymer there are no overlapping confidence intervals. In the case of the determination of 1010 in polypropylene copolymer the 5 and 10 kGy confidence intervals overlap and the 25 and 50 kGy confidence intervals overlap. However, a dose related reduction in the level of antioxidant is still evident. In the case of the determination of 1076 in LDPE the 0 and 1 kGy confidence intervals overlap and the 5 and 10 kGy confidence intervals overlap. However, as with the 1010 determination the dose-related reduction in the level of antioxidant is still apparent.

Although the quality of the statistical results varies, in no case do they cast doubt on the main conclusions of the work. The statistical control of the experiments improved later in the study as would be expected.

3.3 EVIDENCE FOR ELECTRON-BEAM IRRADIATION-INDUCED POLYMER BINDING OF ANTIOXIDANT FRAGMENTS

As detailed in section 1.4 it is possible for fragments of antioxidants to become covalently bound to the polymer during the stabilizing action of the antioxidant. This has been shown by Koch [8] and Smith.[1]

The effects of electron-beam irradiation on the polymer binding of antioxidant fragments occuring in a polypropylene sample containing 0.20% by weight of ^{14}C labelled Irganox 1076 and an HDPE sample containing 0.19% by weight of ^{14}C labelled Irganox 1076 were determined using the method detailed in section 2.11. The samples were subjected to the usual range of irradiation doses.

The results showing the levels of non-extractable ^{14}C activity in the polymer samples, given as percentages of the activity present in the appropriate unextracted non-irradiated sample, are contained in table 3.8 along with the results previously obtained for gamma irradiated samples.[1]

TABLE 3.8

A COMPARISON OF THE EFFECTS OF ELECTRON-BEAM AND GAMMA IRRADIATION ON THE LEVELS OF NON-EXTRACTABLE ^{14}C ACTIVITY (% of activity in the unextracted, non-irradiated, sample)

POLYMER SAMPLE	HDPE + 0.19% ^{14}C-IRGANOX 1076		PP + 0.20% ^{14}C-IRGANOX 1076		
IRRADIATION TYPE / DOSE /kGy	ELECTRON -BEAM	GAMMA	ELECTRON -BEAM 1	ELECTRON -BEAM 2	GAMMA
0	0.27	1.7	0.13	0.13	0.4
1	0.44	N/A	0.17	0.18	N/A
5	0.61	N/A	0.34	0.26	N/A
10	1.29	6.3	0.46	0.37	3.7
25	2.97	11.3	1.05	0.83	7.8
50	4.66	21.8	1.91	1.54	24.1

N/A = No analysis carried out

The conclusions which can be drawn are as follows :

a) There is a dose-related increase in the amount of covalent binding of antioxidant fragments occurring. This is presumably due to the fact that increasing the irradiation dose increases the number of radical sites available for covalent binding with the antioxidant fragments.

b) The percentage of non-extractable, antioxidant derived, material is relatively small. This confirms the need to identify and quantify the extractable antioxidant transformation products.

c) Both electron-beam and gamma irradiation lead to an increase in the extent of covalent binding with dose.

The results showing the levels of extractable ^{14}C activity in the polymer samples, given as percentages of the extractable activity in the unirradiated samples, are contained in table 3.9 along with the results previously obtained for gamma irradiated samples.[11]

TABLE 3.9

A COMPARISON OF THE EFFECTS OF ELECTRON-BEAM AND GAMMA IRRADIATION ON THE LEVELS OF EXTRACTABLE ^{14}C ACTIVITY

(% of extractable activity in the non-irradiated sample)

POLYMER SAMPLE	HDPE + 0.19% ^{14}C-IRGANOX 1076		PP + 0.20% ^{14}C-IRGANOX 1076		
IRRADIATION TYPE / DOSE /kGy	ELECTRON -BEAM	GAMMA	ELECTRON -BEAM 1	ELECTRON -BEAM 2	GAMMA
0	100	100	100	100	100
1	106	N/A	117	103	N/A
5	90	N/A	94	77	N/A
10	80	77	112	85	92
25	52	63	95	80	83
50	39	28	76	66	58

N/A = No analysis carried out

Due to the results of the first determination involving polypropylene being inconsistent with the results contained in table 3.8, in that they did not show the expected dose-related reduction in the levels of extractable ^{14}C activity, the determination, subsequent to the irradiation stage, was repeated. However, the second set of results showed the same inconsistency.

Two possible explanations for this phenomenon were suggested :

i) Gross inhomogeneity within the original polymer sheet from which the samples were cut prior to irradiation.
ii) The irradiation doses received were not as stated.

Both of these possibilities seem unlikely since the levels of unextractable ^{14}C activity show a clear trend and Viritech Ltd operate a strict dose assurance programme.

Due to a lack of time and the fact that this experiment was not a key part of the work, the cause of the inconsistencies remains unidentified.

The results for the HDPE sample do, however, show a dose-related reduction in the levels of extractable ^{14}C activity. The effect is similar for the two types of irradiation.

It is important to note that the results indicating the levels of unextractable ^{14}C activity cannot be directly compared with those for the levels of extractable ^{14}C activity since it was necessary to use two different counting methods.

The results obtained by counting the stabilized polypropylene samples before extraction showed no consistent trend relating to dose. This indicates that no volatile products containing the ^{14}C label are produced on irradiation of the polymer. This would have led to loss of ^{14}C activity prior to extraction.

3.4 THE EFFECTS OF ELECTRON-BEAM IRRADIATION ON THE EXTENT OF MIGRATION OF ANTIOXIDANTS FROM POLYMERS

The specific migration of both Irganox 1010 and Irganox 1076 from two polymer types, polypropylene and a polypropylene copolymer, was determined using the method detailed in section 2.10. The results are contained in tables 3.10 - 3.13 along with those previously obtained concerning the related effects of gamma irradiation.[1] The migration data are presented in units of mg/dm^2 along with the percentage decrease in migration of the antioxidant caused by the irradiation.

TABLES 3.10 AND 3.11

EFFECT OF IRRADIATION ON THE MIGRATION OF IRGANOX 1076 FROM POLYPROPYLENE (INITIAL CONCENTRATION 0.25% BY WEIGHT)

3.10) HOMOPOLYMER

DOSE /kGy	ELECTRON-BEAM IRRADIATION		GAMMA IRRADIATION	
	1076 MIGRATING / mg/dm²	% DECREASE IN MIGRATION AFTER DOSE	1076 MIGRATING / mg/dm²	% DECREASE IN MIGRATION AFTER DOSE
0	2.0	0	2.6	0
1	2.0	0	N/A	N/A
5	1.9	5	N/A	N/A
10	1.7	15	2.1	19
25	1.5	25	1.3	50
50	1.0	50	0.4	85

3.11) COPOLYMER

DOSE /kGy	ELECTRON-BEAM IRRADIATION		GAMMA IRRADIATION	
	1076 MIGRATING / mg/dm²	% DECREASE IN MIGRATION AFTER DOSE	1076 MIGRATING / mg/dm²	% DECREASE IN MIGRATION AFTER DOSE
0	3.7	0	5.1	0
1	3.5	5	N/A	N/A
5	3.1	14	N/A	N/A
10	2.8	23	4.3	16
25	2.2	40	2.7	47
50	1.6	56	1.3	75

N/A = Not available

TABLES 3.12 AND 3.13

EFFECT OF IRRADIATION ON THE MIGRATION OF IRGANOX 1010 FROM POLYPROPYLENE (INITIAL CONCENTRATION 0.25% BY WEIGHT)

3.12) HOMOPOLYMER

DOSE /kGy	ELECTRON-BEAM IRRADIATION		GAMMA IRRADIATION	
	1010 MIGRATING / mg/dm²	% DECREASE IN MIGRATION AFTER DOSE	1010 MIGRATING / mg/dm²	% DECREASE IN MIGRATION AFTER DOSE
0	0.33	0	0.8	0
1	0.27	18	N/A	N/A
5	0.21	36	N/A	N/A
10	0.17	48	0.3	63
25	0.11	67	<0.2	>75
50	0.06	82	<0.2	>75

3.13) COPOLYMER

DOSE /kGy	ELECTRON-BEAM IRRADIATION		GAMMA IRRADIATION	
	1010 MIGRATING / mg/dm²	% DECREASE IN MIGRATION AFTER DOSE	1010 MIGRATING / mg/dm²	% DECREASE IN MIGRATION AFTER DOSE
0	2.3	0	2.8	0
1	2.1	9	N/A	N/A
5	1.7	26	N/A	N/A
10	1.4	39	1.4	50
25	0.8	65	0.5	82
50	0.4	83	0.3	89

N/A = Not available

From the migration data for the unirradiated samples the following conclusions can be drawn about the migration of these antioxidants into isooctane :-

i) Irganox 1076 migrates from the polymers into isooctane more easily than Irganox 1010, presumably because of its greater lipophilicity arising from the long C_{18} hydrocarbon chain.

ii) The levels of migration from the polypropylene copolymer samples are greater than for the polypropylene homopolymer sample.
This is probably due to the greater degree of crystallinity within the copolymer sample. Since antioxidants are excluded from the crystalline regions [2] this will increase the effective antioxidant concentration in the amorphous regions available to migrate into the isooctane.

The conclusions concerning the effects of irradiation on the migration process are as follows :

a) Electron-beam irradiation causes a dose-related reduction in the extent of migration of both antioxidants.

b) The effects of electron-beam and gamma irradiation on the migration of the antioxidants are broadly similar.

c) The percentage decrease in the levels of antioxidant migrating caused by irradiation are greater for Irganox 1010 than for Irganox 1076. This reflects its greater susceptibility to transformation by irradiation (see section 3.2).

The literature does not appear to contain any references to which these results can be directly compared. The fact that the level of antioxidant migrating decreases in dose-related manner, reduces any health risk which may be presented by the migration of these antioxidants into fatty foods from food-contact polymers.

During this study it was also noted that the extractable transformation products arising from the antioxidants on irradiation, are able to migrate from the polymer into isooctane in a similar manner to the antioxidants themselves. Attempts to identify these transformation products are detailed in chapter 4 and possible structures suggested. An indication of the extent to which these transformation products migrate can be gained by examining the chromatograms recorded. The chromatograms from the analysis to determine the extent of migration of Irganox 1010 from electron-beam irradiated polypropylene copolymer are shown in figure 3.4. Although these transformation products are able to migrate, they are only present at relatively low concentrations after an irradiation dose of 10kGy, the maximum dose permitted by legislation in the UK.

FIGURE 3.4

Chromatograms to indicate the extent of migration of Irganox 1010 transformation products from unirradiated polypropylene copolymer (A) and samples of the same polymer subjected to electron-beam irradiation doses of 10 (B) and 50 (C) kGy. In each case the same amount of 1076 is present as an internal standard allowing direct comparison between the three chromatograms.

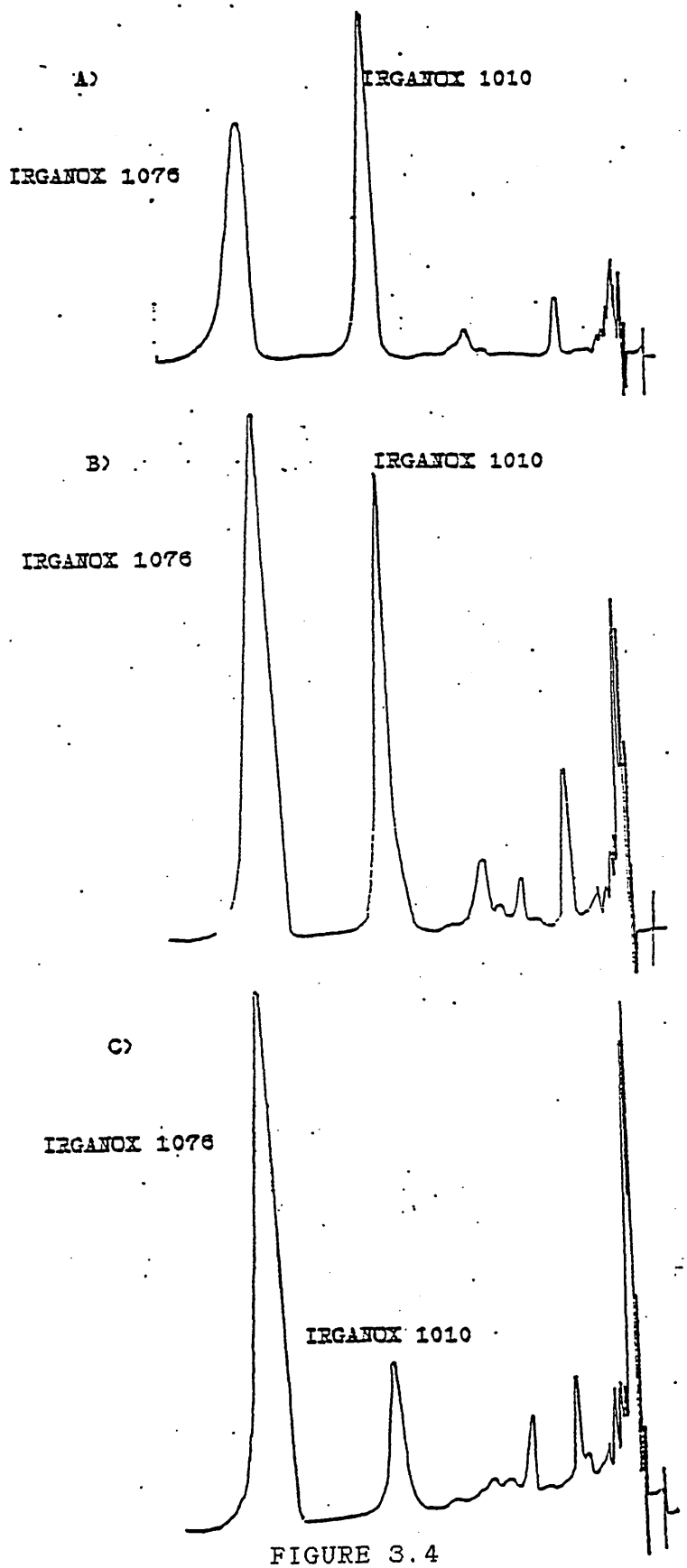
A)
IRGANOX 1010
IRGANOX 1076
B)
IRGANOX 1010
IRGANOX 1076
C)
IRGANOX 1076
IRGANOX 1010

FIGURE 3.4

The fact that the antioxidant transformation products produced by irradiation do migrate from the polymer into the simulants makes their identification even more important. If any of these products prove to be potentially harmful to the consumer, quantitative determination of their migration will be essential.

The results were calculated using the Lotus-123® spreadsheet, as detailed in section 3.2.

For the sake of brevity only a selection of the results calculated are presented here. However, table 3.14 gives the limits of detection for each of the migration analyses along with 50kGy results with their 95% Confidence Limits.

Although the quality of the statistical results varies, in no case do they cast doubt on the main conclusions of the work.

TABLE 3.14

LIMITS OF DETECTION AND 95% CONFIDENCE LIMITS

FOR THE ELECTRON-BEAM 50kGy RESULTS

OF THE MIGRATION ANALYSES

MIGRATION ANALYSIS	LIMIT OF DETECTION / mg dm^{-2}	50kGy RESULT WITH 95% CONFIDENCE LIMITS
1010 from PP(H)	0.025	0.058 +/- 0.015
1010 from PP(C)	0.034	0.437 +/- 0.021
1076 from PP(H)	0.30	1.01 +/- 0.18
1076 from PP(C)	0.26	1.63 +/- 0.15

3.5 THE EFFECTS OF GAMMA IRRADIATION ON THE LEVEL OF TINUVIN 622 IN POLYPROPYLENE

The literature appears to contain no references to the effects of irradiation on Tinuvin 622 in polymers. It was therefore decided to start by investigating the effects of gamma irradiation on Tinuvin 622 in polypropylene. Since Tinuvin 622 is a polymeric stabilizer, (fig 1.4), it is not possible to determine it directly by readily available chromatographic techniques. However, it was decided that it may be possible to detect some irradiation-produced transformation products arising from Tinuvin 622 using the same hplc method as that used for phenolic antioxidants detailed in section 2.8. The following study was carried out:-

Polypropylene containing Tinuvin 622 at an initial concentration of 0.2% by weight was subjected to gamma irradiation doses of 1, 5, 10, 25 and 50kGy. These samples and an unirradiated batch of polymer were extracted and analysed in the usual way using Irganox 1076 as an internal standard. A control experiment consisting of heating Tinuvin 622 under reflux in 1,1,1-trichloroethane, without any polymer present, was also carried out. HPLC analysis of this sample revealed no peaks after 20 minutes.

The hplc trace of the non-irradiated sample revealed the presence of at least six Tinuvin 622 transformation products which were almost certainly produced by the initial thermal processing. Four of these peaks were still

present after a dose of 50kGy; however, these products were not fully separated from the solvent front. The other two products were separated from the solvent front.

It was possible to estimate the effect of gamma irradiation on the amount of the latter two products in the polypropylene samples by using the ratio of each peak height to that of the internal standard. This semi-quantitative data is presented in table 3.15.

The amount of the earlier product is first increased and then decreased by irradiation whilst the extent of the latter product is progressively decreased by irradiation. There is no trace of either product in extracts of samples subjected to doses of 25 or 50 kGy.

The fact that irradiation causes the production of some transformation products indicates that the level of Tinuvin 622 present is reduced by irradiation. Obviously further work in this area is required. All the transformation products have yet to be identified, attempts to do this are detailed in chapter 4, and further quantitative analysis of such products is required. The chromatographic conditions could be improved and other instrumental techniques, more suited to the determination of Tinuvin 622, could be used (see section 2.5). The effect of electron-beam irradiation on Tinuvin 622 could also be determined. However, time did not permit this work to be carried out during the present study.

TABLE 3.15

RESULTS FOR THE DETERMINATION OF TINUVIN 622 TRANSFORMATION PRODUCTS IN IRRADIATED POLYPROPYLENE

DOSE /kGy	% of 72mm peak remaining	% of 110mm peak remaining
0	100	100
1	157	72
5	102	26
10	107	28
25	0	0
50	0	0

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CHAPTER 4 - THE IDENTIFICATION OF TRANSFORMATION PRODUCTS OF ANTIOXIDANTS AND HALS

4.1 INTRODUCTION

During the hplc investigation to determine the effects of electron-beam irradiation on the levels of antioxidants in polyolefins, many irradiation-produced antioxidant transformation products were detected. In order to ensure public safety it is obviously necessary to determine the identity of these products.

The analytical techniques used to further this aim were gas chromatography with flame ionization or mass spectrometry detectors, high performance liquid chromatography using a UV/VIS multichannel detector or linked to a mass spectrometer, ^{1}H nmr spectroscopy and finally, in the case of the antioxidant Irgafos 168, ^{31}P nmr spectroscopy.

Thermal aging of polypropylene containing antioxidants was also carried out in order to determine whether thermal oxidation and irradiation of stabilized polymers produce the same range of transformation products.

Several model reactions were also carried out involving the reaction of the antioxidants with tert-butylperoxyl radicals. In addition the oxidation of Irganox 1010 and Irganox 1076 was carried out using potassium hexacyanoferrate (III). Thus a comparison could be drawn

between the products formed by these reactions and those produced by irradiation.

These investigations are detailed for each antioxidant in sections 4.2 - 4.5 respectively. Section 4.6 details attempts to identify transformation products of the hindered amine light stabilizer Tinuvin 622.

Unless otherwise stated the extracts used for these investigations were prepared from polypropylene, stabilized by the additive in question, subjected to an irradiation dose of 50kGy. 10g of irradiated stabilized polymer was extracted in the usual way, the final volume of the extract being about 0.5ml. Thus the extracts used for this purpose were more concentrated than those used during the work detailed in chapter 3.

4.2 TRANSFORMATION PRODUCTS OF IRGANOX 1010

The isocractic hplc chromatogram of the extract from polypropylene stabilized by Irganox 1010 subjected to an irradiation dose of 50kGy is displayed in figure 4.1. At least twelve different transformation products are present in the extract, and there are almost certainly other products which appear together at the solvent front, judging from the long wavelength absorption detected therein.

The UV spectra of the five transformation products with the greatest absorbances at 275nm are shown in figure 4.2 along with that of Irganox 1010 itself.

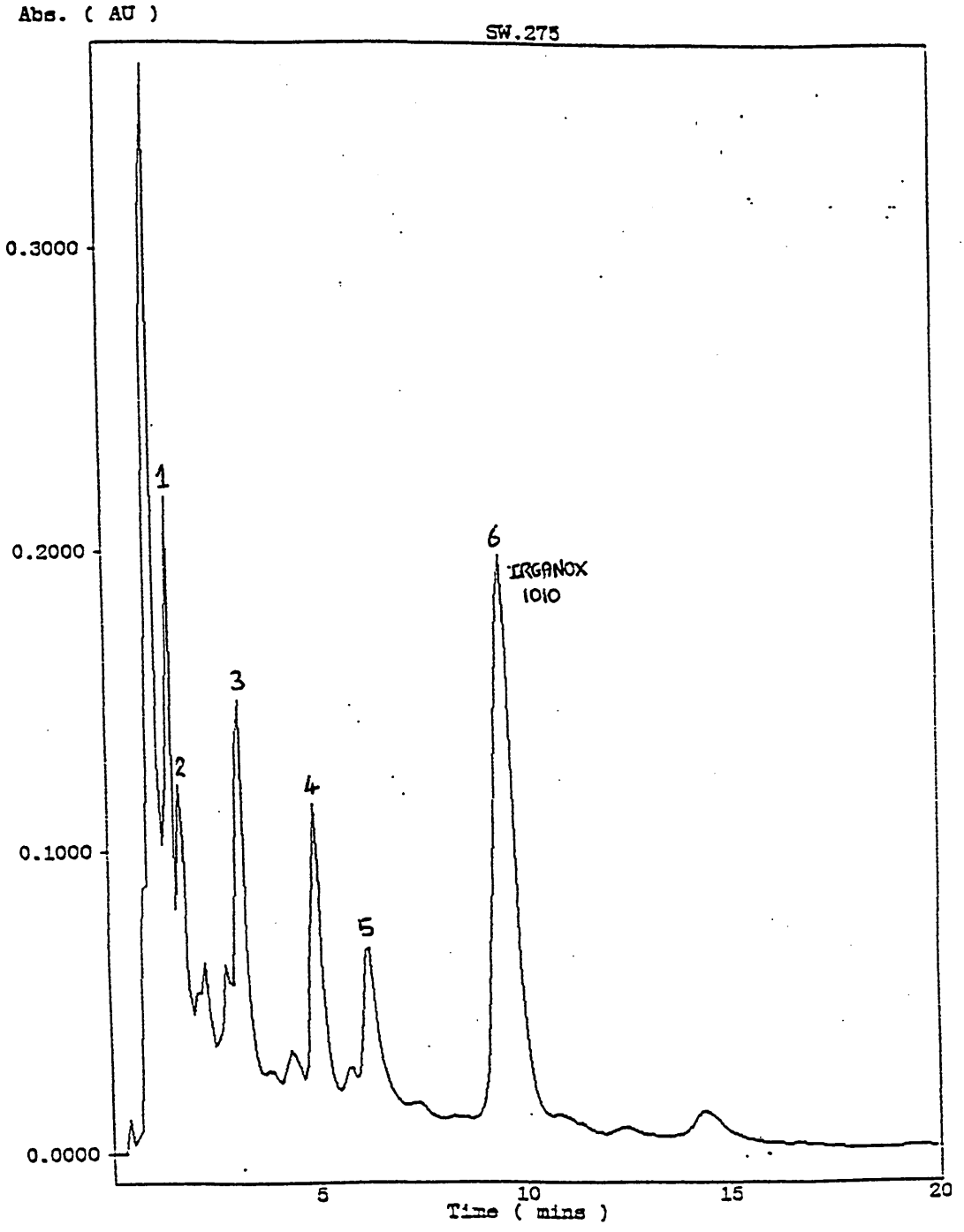


FIGURE 4.1. Isocratic hplc chromatogram of the extract from polypropylene homopolymer stabilized by Irganox 1010, subjected to an irradiation dose of 50kGy.

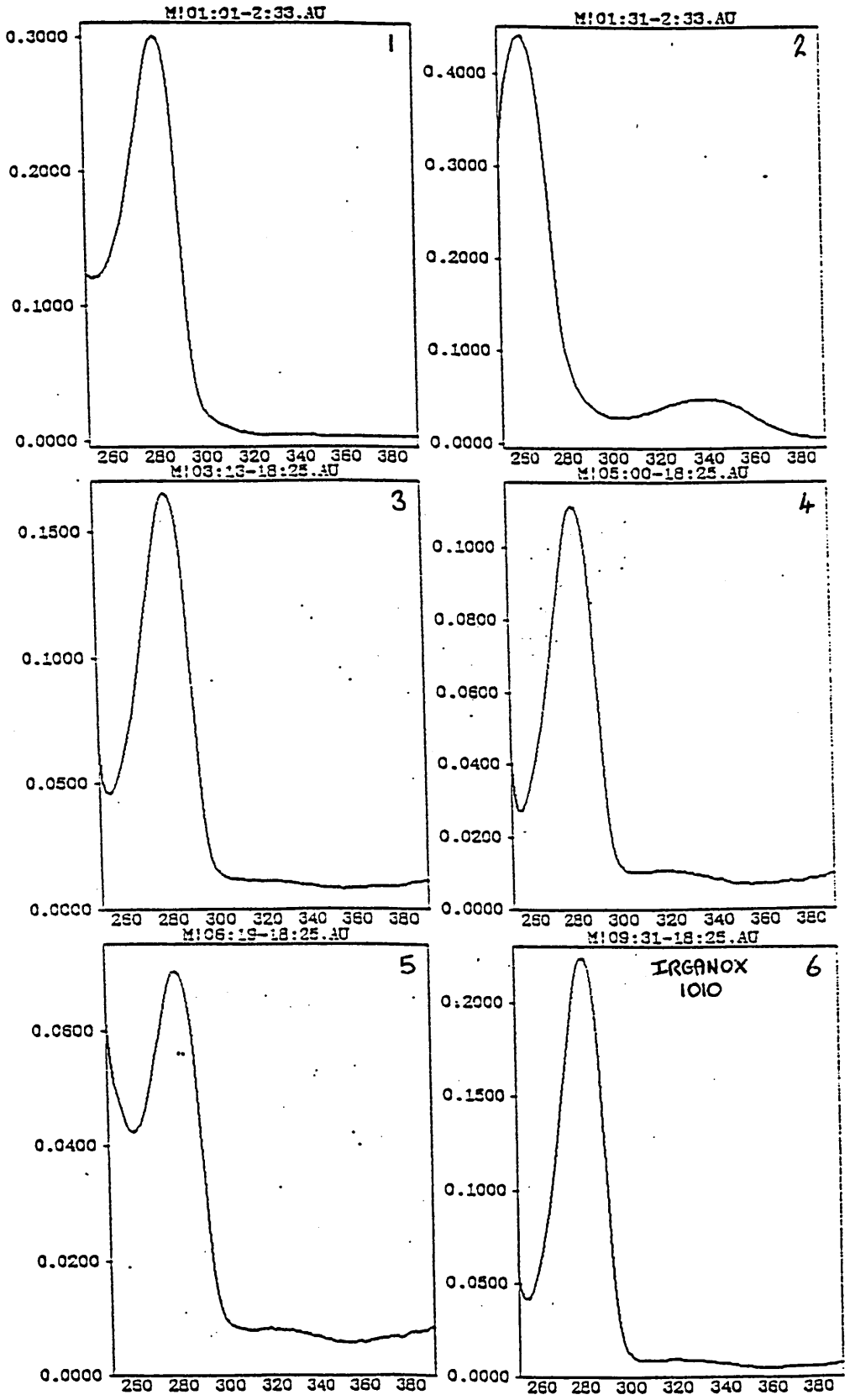


FIGURE 4.2. UV Spectra of Irganox 1010 and its principal irradiation-derived transformation products.

The spectrum for component 1 shows an absorption maximum at a similar position to that of Irganox 1010. This indicates that this compound retains one or more phenolic units from the Irganox 1010 structure. It also shows some absorbance above 300nm. This probably indicates the presence of some conjugation but certainly not of cinnamate functionalities which would absorb strongly with maxima at about 320nm. The spectrum for component 2 shows an absorption maximum at about 260nm in contrast to that of Irganox 1010, for which λmax = 282nm. This absorption is probably due to carbonyl groups present in quinonoid functionalities. The absence of an absorbance maximum at about 280nm probably indicates the lack of phenolic units such as those present in Irganox 1010. The presence of a less intense absorption at about 326nm indicates the presence of conjugated and possibly quinonoid type character. In fact the spectrum of component 2 is very similar to that of 2,6-di-t-butylbenzoquinone and its retention time is also similar. It is therefore reasonable to conclude that this product is 2,6-di-t-butylbenzoquinone, which is known to arise by oxidation of this type of antioxidant. Components 3 to 5 all have similar UV spectra to Irganox 1010, with absorbance maxima at about 280nm. This probably indicates the presence of one or more phenolic units of the type contained in Irganox 1010. Any absorption resulting in peak maxima at about 256nm is probably due to $\pi \rightarrow \pi^*$ transition taking place in the aromatic ring. None of these three compounds

have UV absorbances indicative of quinonoid or cinnamate functionalities.

Oxidative chemistry would be expected to result in the formation of quinonoid or cinnamate units as indicated by Pospisil in scheme 1 (see section 1.4).[1] This suggests that oxidative chemistry is not the predominant process occuring when polypropylene containing Irganox 1010 is subjected to irradiation.

None of the irradiation-derived transformation products arising from Irganox 1010 were detected by the gas chromatographic methods described in sections 2.6 and 2.7. The reason why 2,6-di-t-butylbenzoquinone was not detected is unclear. It was detected in other extracts and may have been obscured by peaks due to polypropylene oligomers in this case. These results probably indicate that the transformation products are of low volatility, which may be due to their high relative molecular masses or high polarities.

Using the gradient hplc system, detailed in section 2.8, revealed that the situation is much more complex and there are many other transformation products formed in addition to those already noted. The chromatogram at 275nm produced using this system is presented in figure 4.3.

An hplc-ms investigation of this extract was carried out according to the method detailed in section 2.9. The resulting total ion chromatogram (TIC) is contained in figure 4.4.

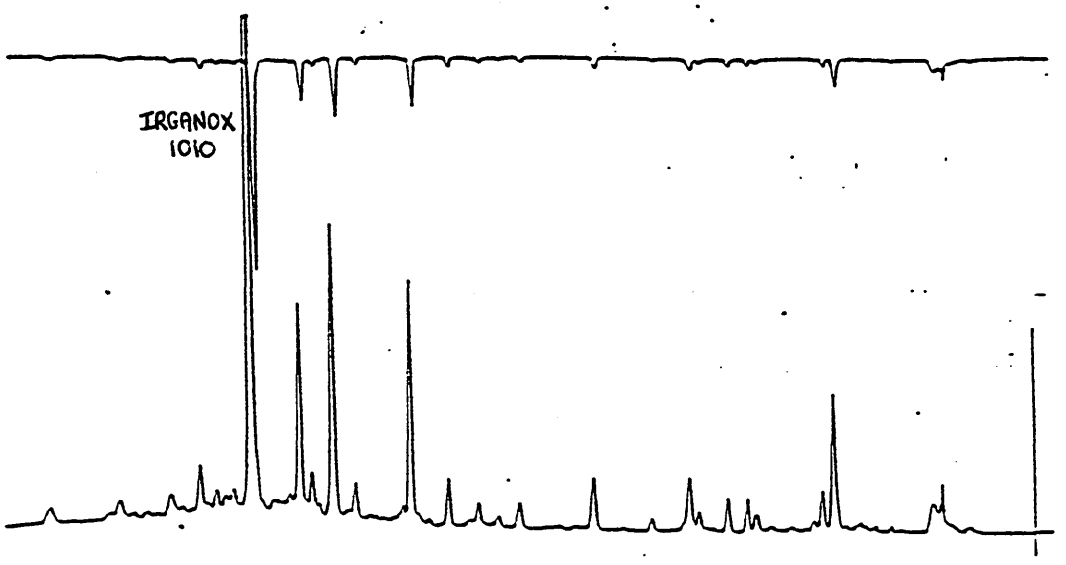


FIGURE 4.3. Gradient hplc chromatogram of the extract from polypropylene homopolymer stabilized by Irganox 1010, subjected to an irradiation dose of 50kGy.

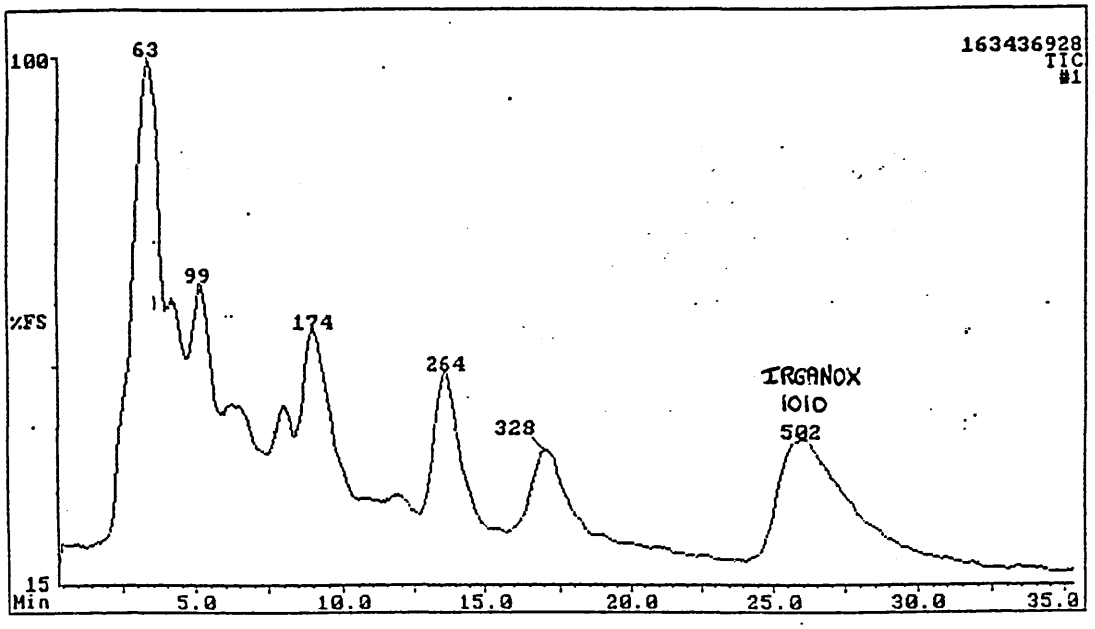
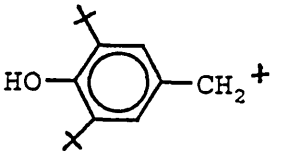


FIGURE 4.4. LC-MS TIC of the extract from polypropylene homopolymer stabilized by Irganox 1010, subjected to an irradiation dose of 50kGy.

The TIC compares well with the chromatogram obtained by UV detection at 275nm giving an indication of the efficiency of the particle-beam interface. The peak heights give a better indication of the relative amounts of each product present than do those obtained using UV detection. This is because the TIC, as its name suggests, reflects the abundance of ions generated, whilst the height of the peaks from UV detection is dependent upon the molar absorption coefficient of the compound. However, ions above the scanning range of 1000 mass units will not be detected, which of course will affect the TIC peak height obtained for Irganox 1010 (RMM = 1178).

A selection of the mass spectra which show clear molecular ions, obtained from this experiment, are presented in figure 4.5. Irganox 1010 will not, of course, show a molecular ion, since its relative molecular mass of 1178 is above the mass range of the spectrometer. The molecular mass of the product at scan number 328 also remains unclear.

These spectra all show the presence of a characteristic fragment with a mass of 219 which is probably due to fragment (I).

fragment (I) 

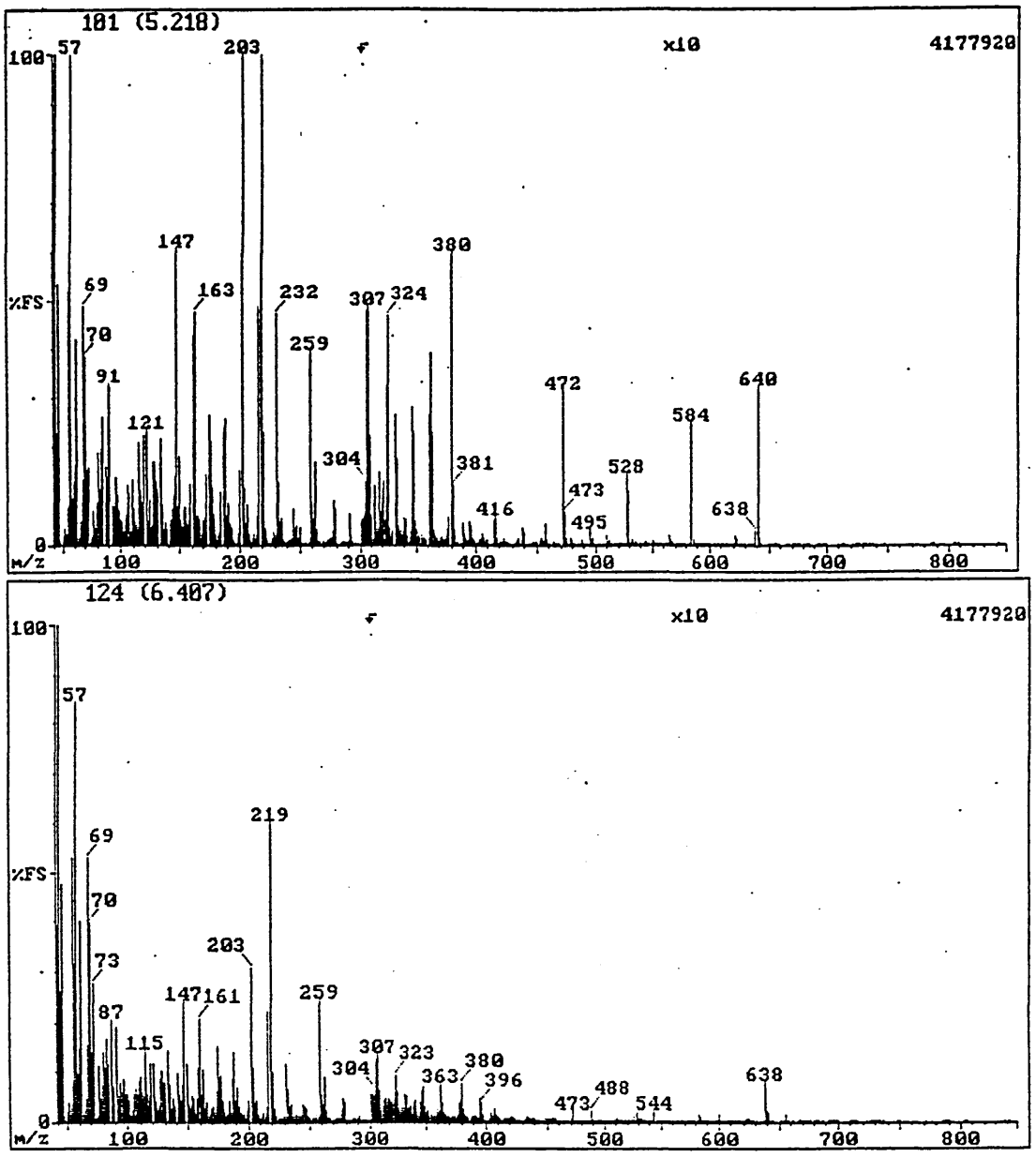
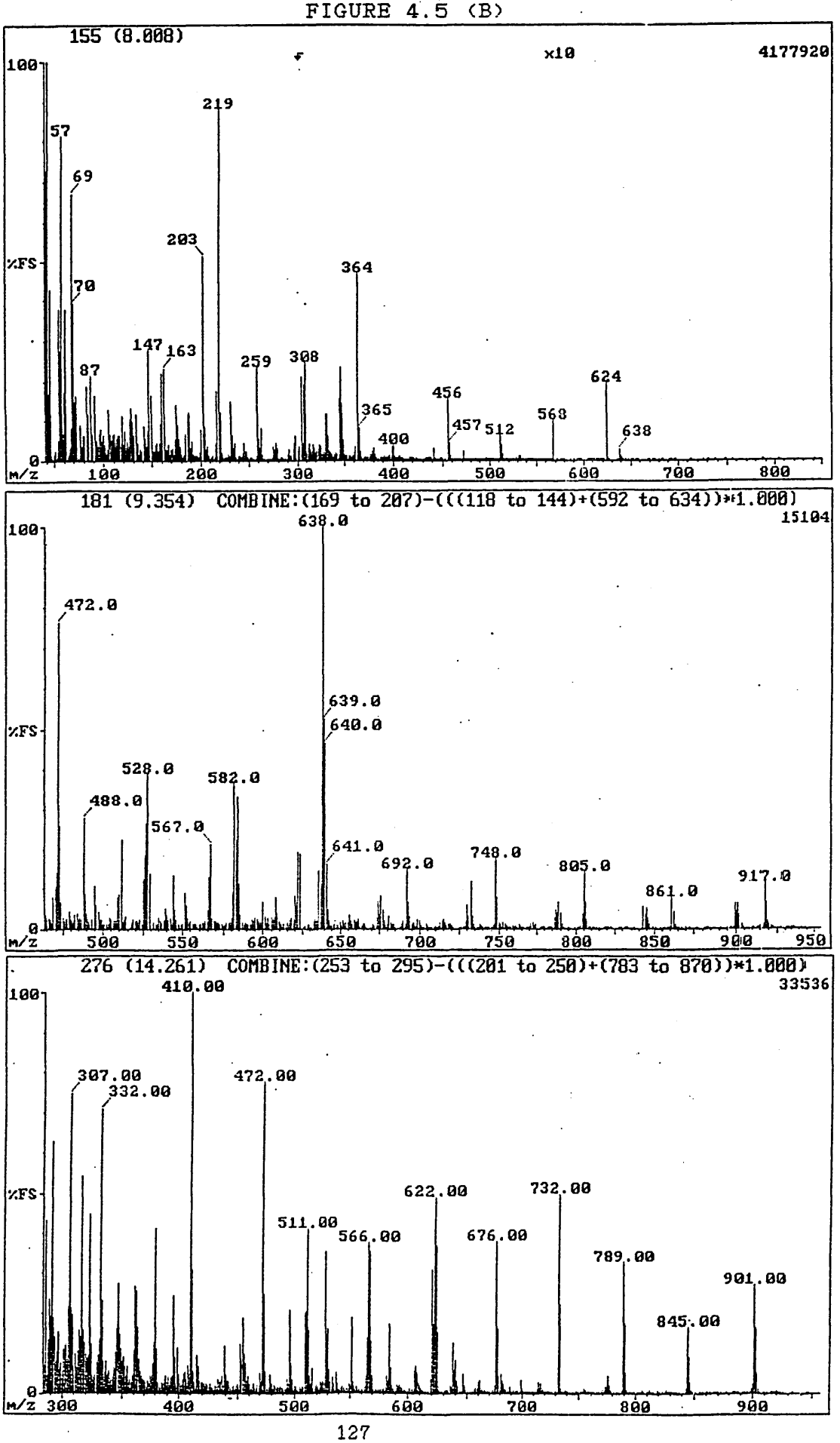


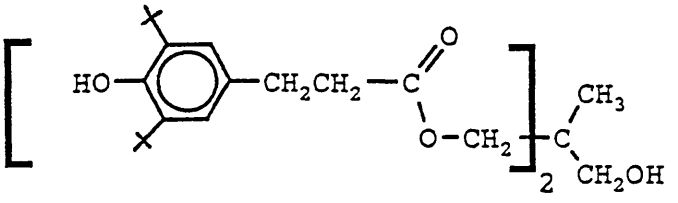
FIGURE 4.5 (A) Mass spectra obtained for some irradiation -derived transformation products of Irganox 1010.

FIGURE 4.5 (B)

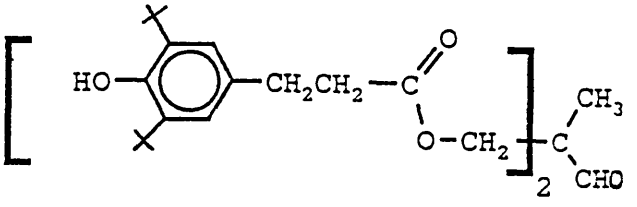

155 (8.008)
x10
4177920
100
%FS
0
m/z
57
69
70
87
147
163
203
219
259
308
364
365
400
456
457
512
563
624
638
100
200
300
400
500
600
700
800
181 (9.354) COMBINE:(169 to 207)-(((118 to 144)+(592 to 634))*1.000)
15104
638.0
472.0
639.0
640.0
528.0
582.0
488.0
567.0
641.0
692.0
748.0
805.0
861.0
917.0
500
550
600
650
700
750
800
850
900
950
276 (14.261) COMBINE:(253 to 295)-(((201 to 250)+(783 to 870))*1.000)
33536
410.00
307.00
332.00
472.00
622.00
732.00
511.00
566.00
676.00
789.00
901.00
845.00
300
400
500
600
700
800
900

They also show the characteristic loss of 56 mass units which is due to the loss of C_4H_8 a neutral molecule from the tertiary-butyl groups.

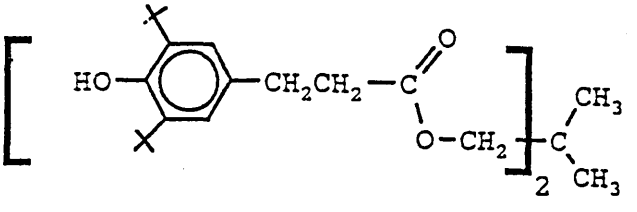
Using these data the following structures, which are consistent with the UV spectra obtained, are proposed for some of the transformation products.



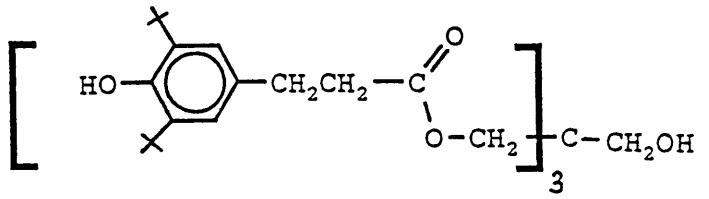
RMM = 640, suggested for the product at scan number 101



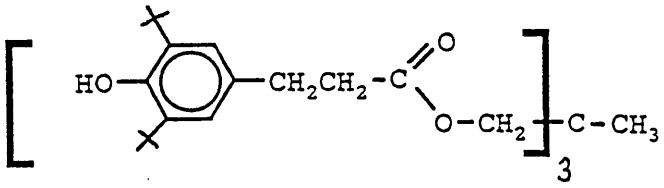
RMM = 638, suggested for the product at scan number 124



RMM = 624, suggested for the product at scan number 155



RMM = 917, suggested for the product at scan number 181



RMM = 901, suggested for the product at scan number 276

It should be possible to confirm whether these structures are correct by collecting the appropriate components in fractions recovered from the hplc waste pipe. The solvents can then be removed by freeze drying and the solid samples analysed using nmr spectroscopy. This procedure was carried out and the purity of the fractions was confirmed using hplc. Six peaks including that for Irganox 1010 were collected. The chromatogram from which they were collected is displayed in figure 4.6. The components collected are numbered 1 - 6 with component 6 being Irganox 1010. The ^1H nmr spectra obtained are displayed in figure 4.7 along with that of pure Irganox 1010 and the conclusions which can be drawn are as follows :-

The ^1H nmr signals can be assigned in the following way, consistent with Irganox 1010 and similar structures:-

Signal A - C_4H_9 - this signal for the t-butyl groups appears to be split in some cases. The reason for this is unclear.

Signal B - Ar-H

Signal C - Ar-OH

Signal D - Ar-CH_2CH_2-COO-

Signal E - COO-CH_2-C- - this signal could be masked in some cases by signals due to the unremoved ethyl acetate solvent.

A number of signals in the spectra contained in figure 4.7 can be assigned to solvents which are present, and the internal standard :-

Signal S1 - this is due to the hydrogen atom in chloroform, traces of which are present in the deuteriochloroform solvent used for nmr analyses.

Signal S2 - artifacts due to the solvents present.

Signal S3 - these are due to unremoved ethyl acetate.

Signal S4 - these are due to unremoved methanol.

Signal S5 - due to the TMS internal standard marking δ = 0 ppm

Four other signals remain unassigned :-

Signal U1 - probably an artifact.

Signal U2 - unidentified but not diagnostic since it is common to fractions 1, 3, 4, 5 and 6.

Signal U3 - unidentified but could be due to oligomer impurities in the samples, however this is not certain and this signal could be significant. This signal is sometimes masked by the one of of the ethyl acetate signals.

Signal U4 - unidentified signal.

The relationship between the integral heights was not clear and could not be used diagnostically. It is clear that more of each sample should have been collected to improve the intensity of the signals and that the hplc solvents must be completely removed to avoid them masking smaller signals. Obviously this procedure needs to be repeated more carefully taking these factors into account. However it is important to note that, although there are no signals which clearly confirm the proposed structures, there are no signals present which clearly contradict the proposed structures, such as signals due to quinonoid or cinnamate functionalites.

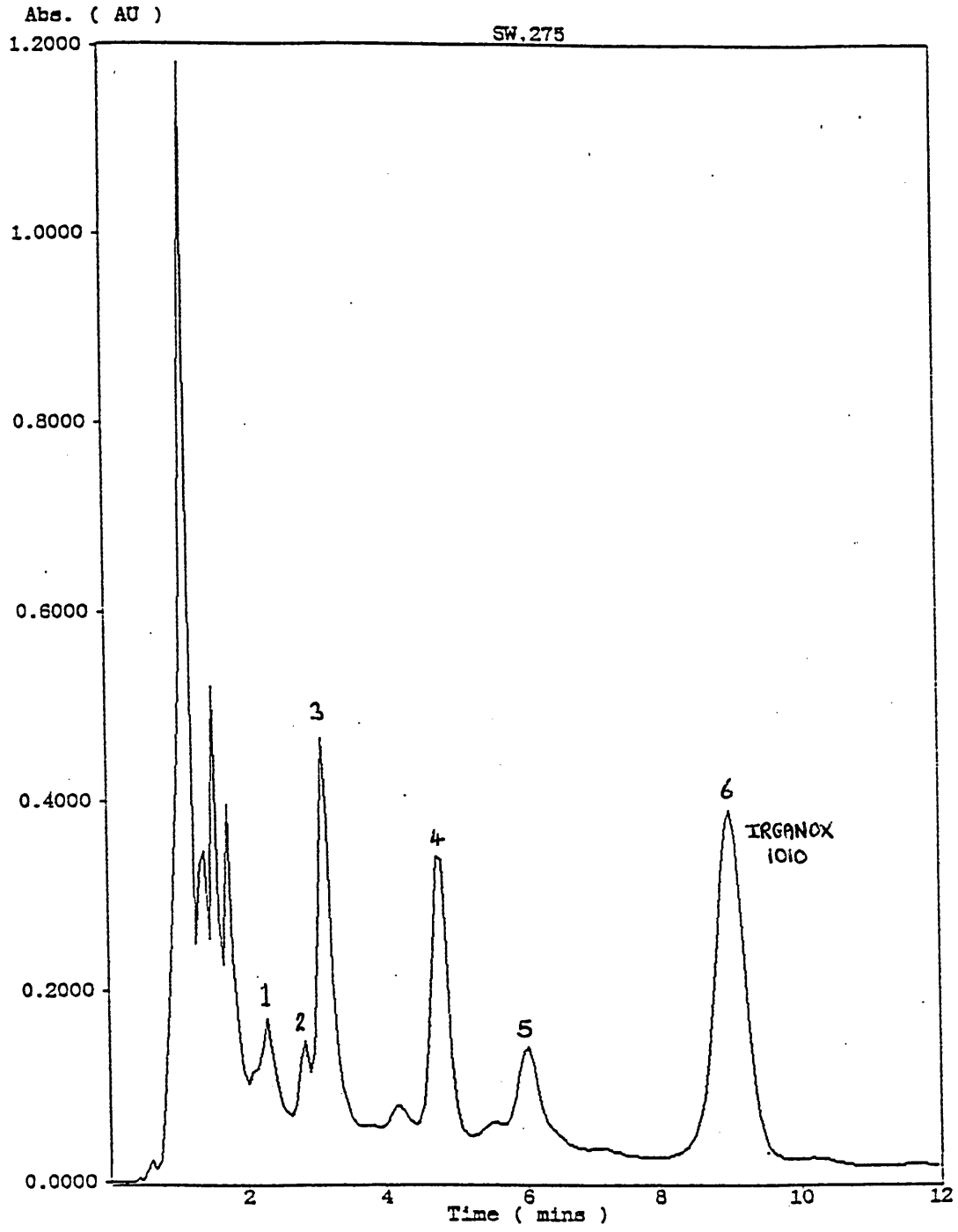
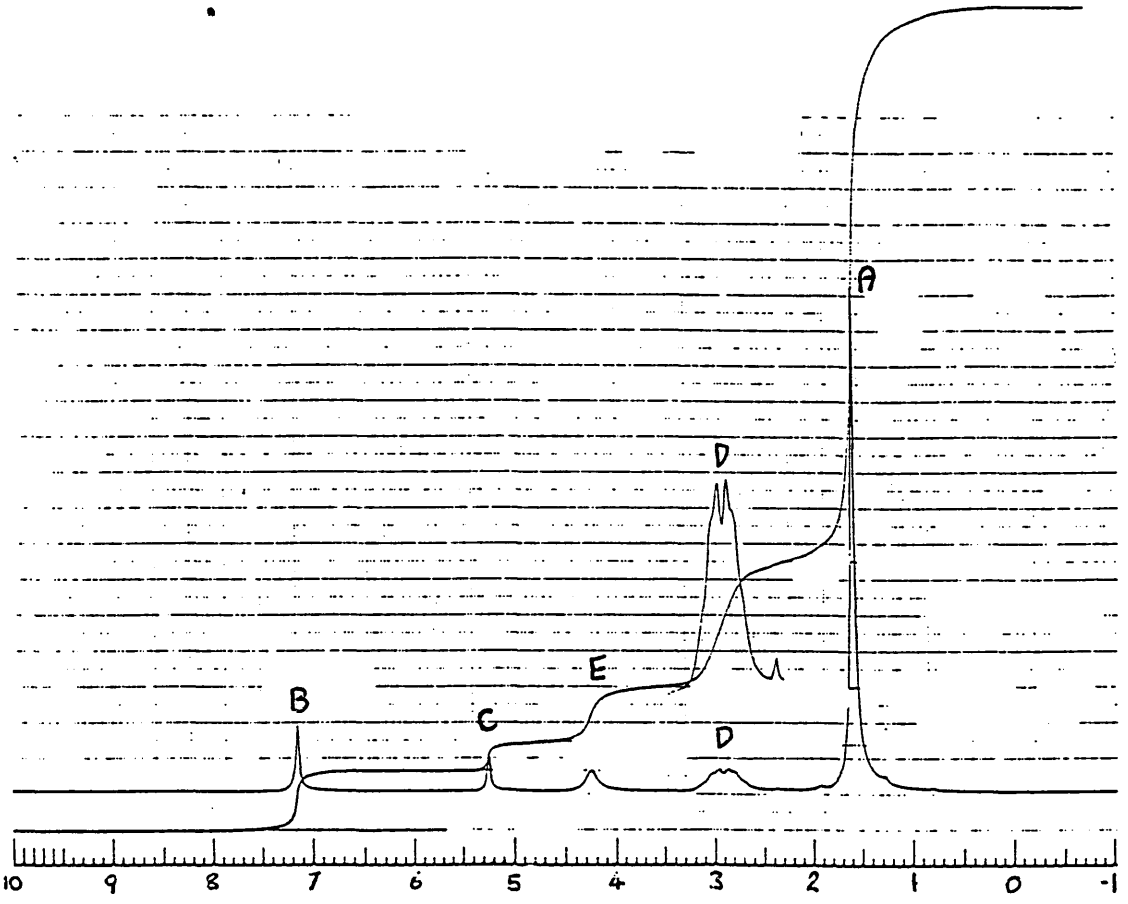
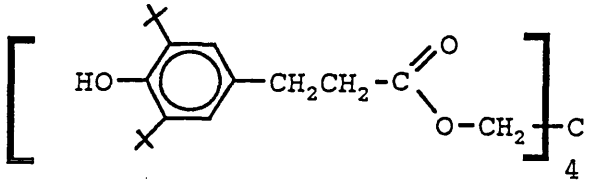


FIGURE 4.6. Isocratic hplc chromatogram of the extract from polypropylene homopolymer stabilized by Irganox 1010, subjected to an irradiation dose of 50kGy.



δ /ppm

FIGURE 4.7 (A) ^1H nmr spectrum of authentic Irganox 1010.



A ≡ $-C_4H_9$

B ≡ -Ar-H

C ≡ -Ar-OH

D ≡ $-Ar-CH_2CH_2-COO-$

E ≡ $-COO-CH_2-C-$

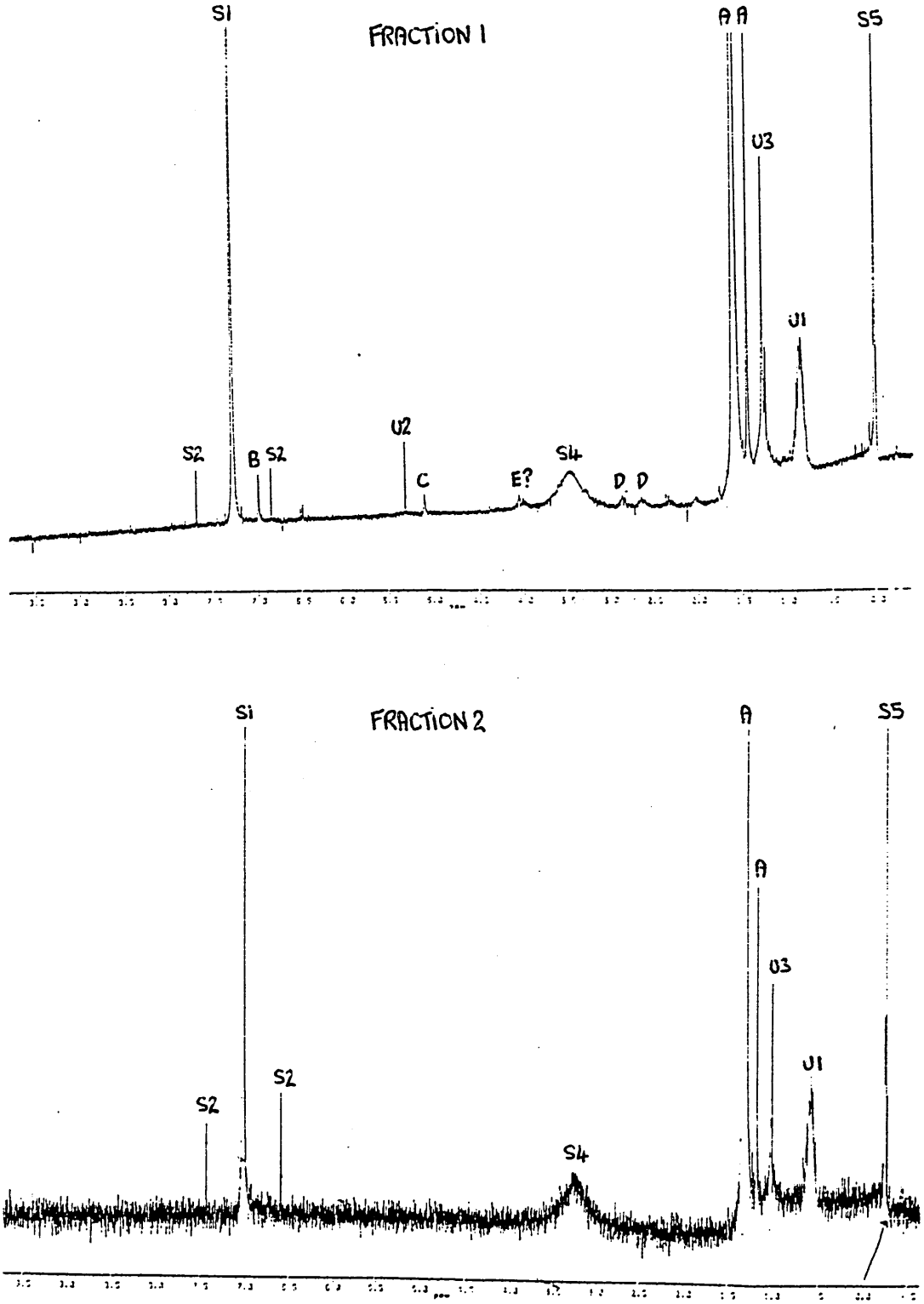


FIGURE 4.7 (B) ^{1}H nmr spectra for fractions 1 and 2.

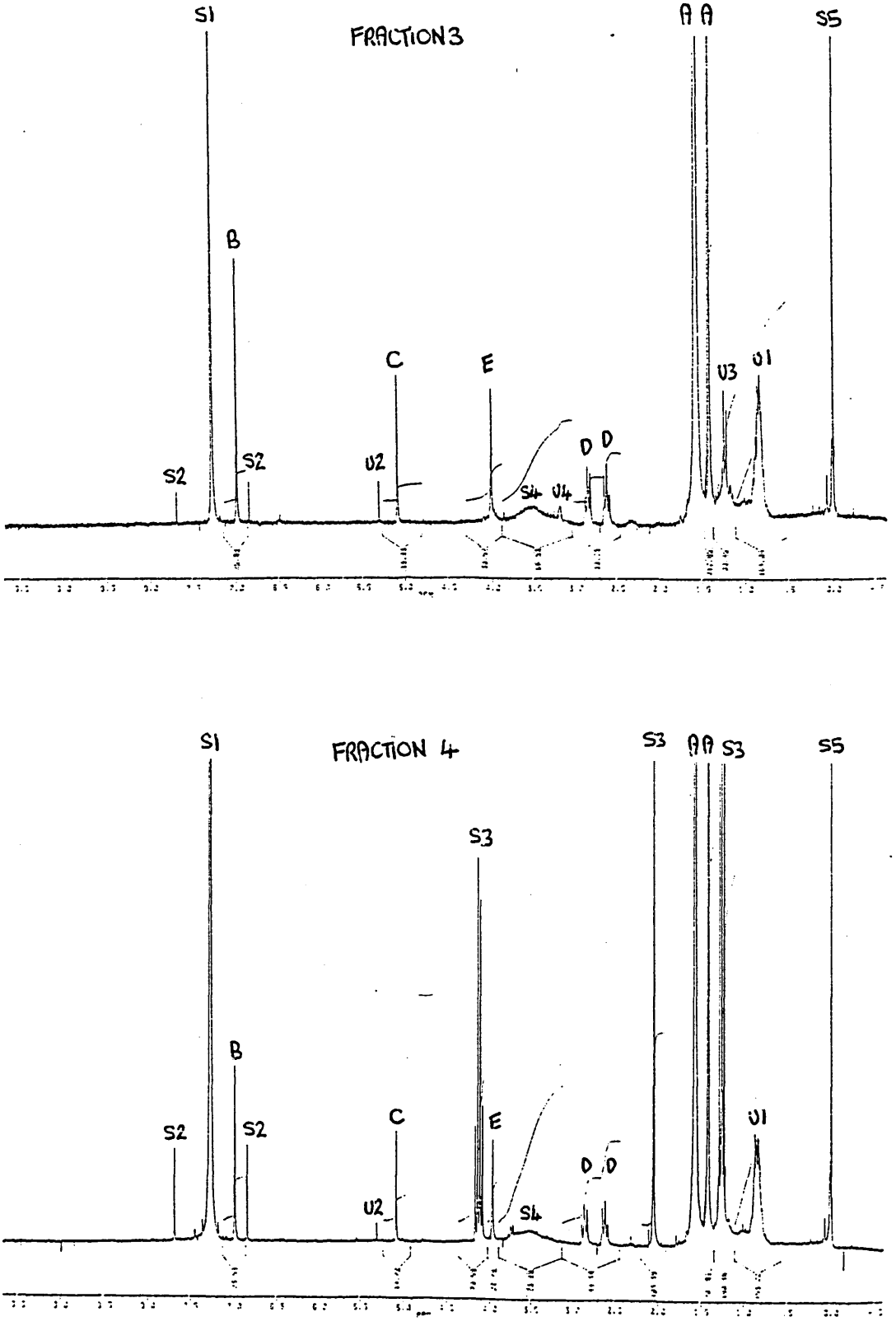


FIGURE 4.7 (C) ^{1}H nmr spectra for fractions 3 and 4.

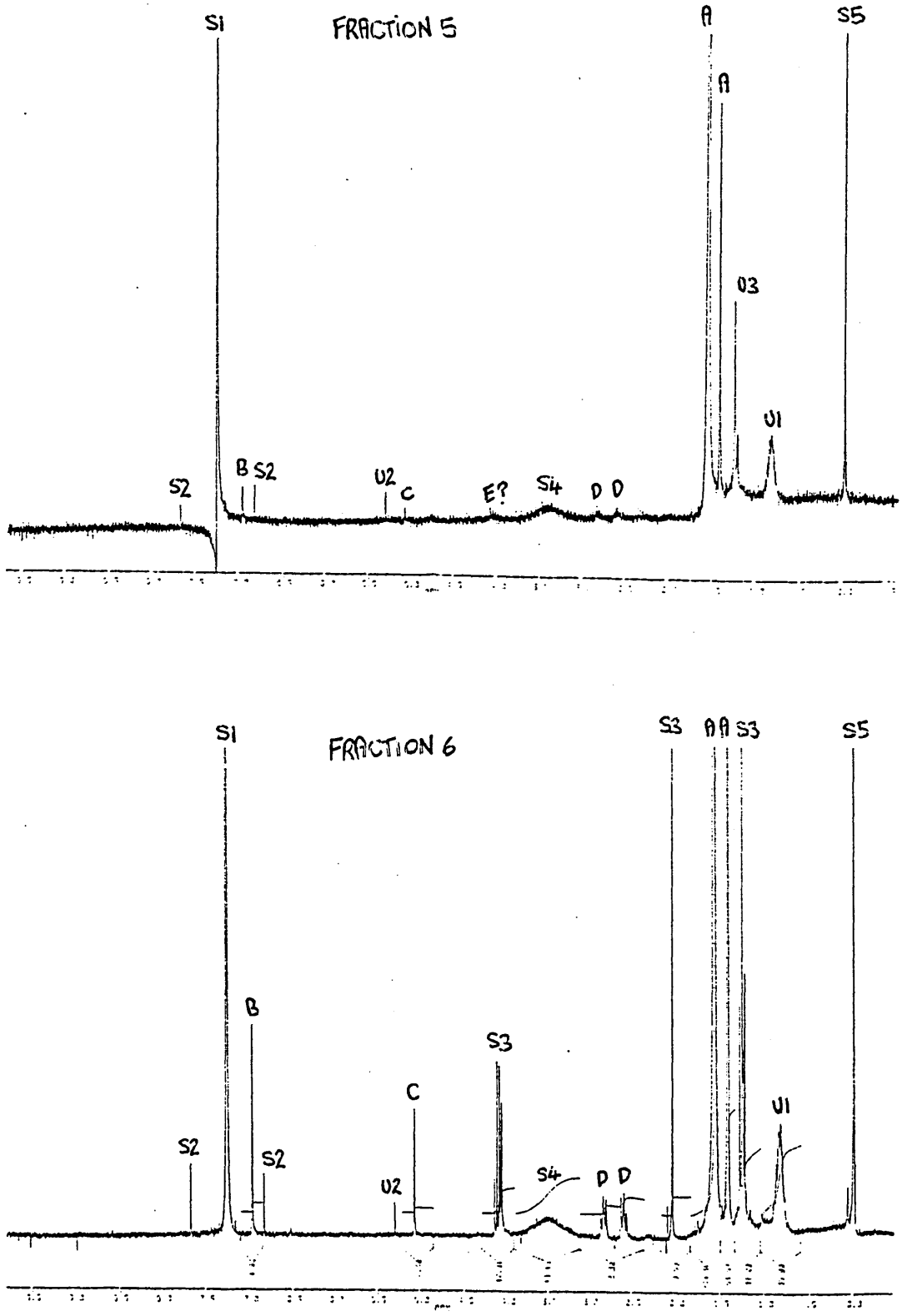


FIGURE 4.7 (D) ^{1}H nmr spectra for fractions 5 and 6.

A sample of polypropylene stabilized by Irganox 1010 was subjected to the thermal aging process detailed in section 2.12.

The isocratic hplc chromatogram for the resulting extract, produced using the method detailed in section 2.8, is contained in figure 4.8. Similar chromatograms for extracts from the same polymer before either irradiation or thermal treatment and after an irradiation dose of 50kGy are also displayed in figure 4.8 for comparison.

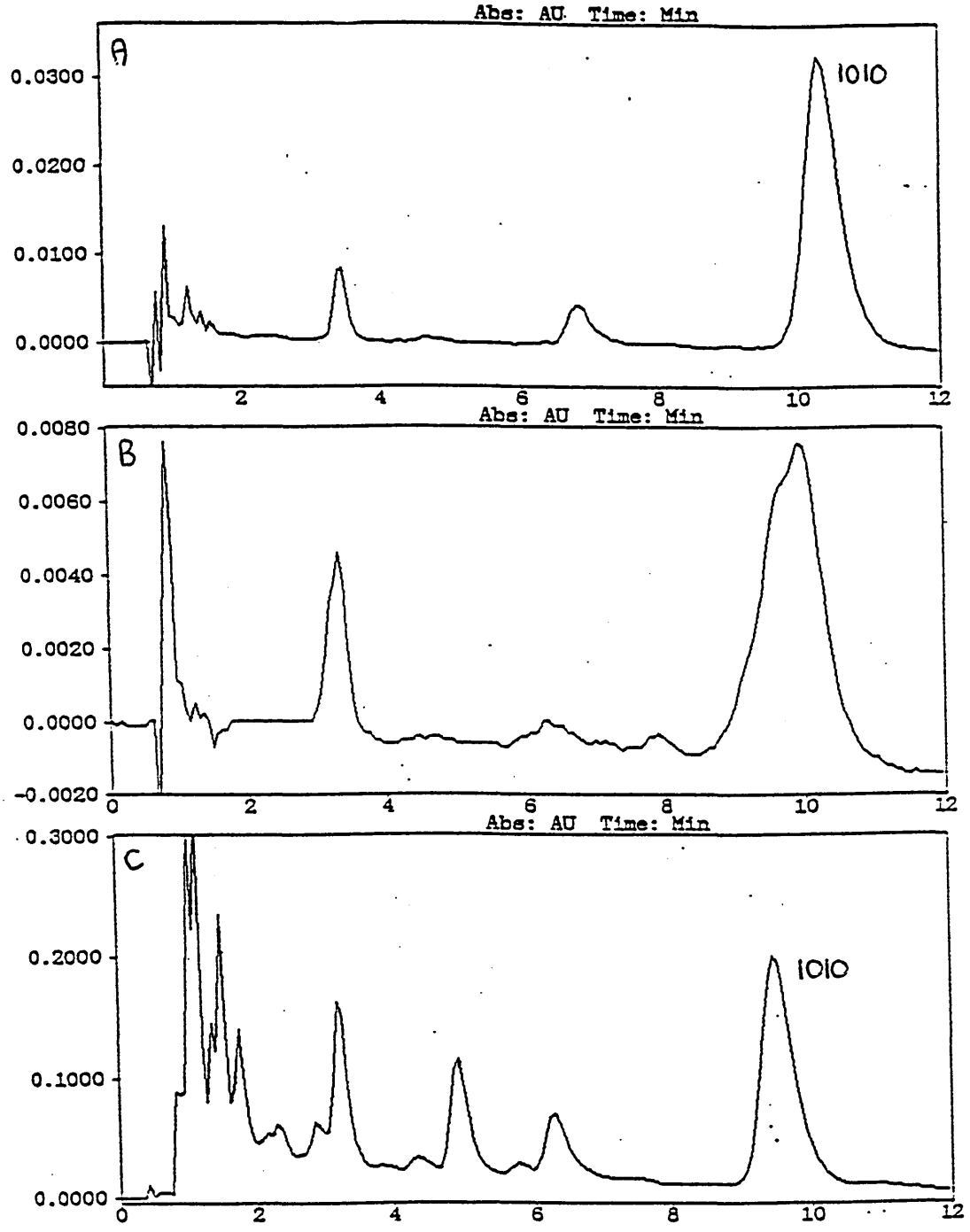


FIGURE 4.8 A) Hplc chromatogram of the extract from 0kGy PP(H) containing 1010
- no thermal treatment.
B) Hplc chromatogram of the extract from 0kGy PP(H) containing 1010
- after 400 hours at 150°C
C) Hplc chromatogram of the extract from 50kGy PP(H) containing 1010
- no thermal treatment

The retention times for the Irganox 1010 peaks on the three chromatograms do not coincide exactly because the samples were not chromatographed consecutively.

The chromatogram from the untreated polymer clearly shows the Irganox 1010 peak, which was shown to be pure by examining the UV spectrum at various intervals across the peak. There are also some minor transformation products which are almost certainly produced during the initial thermal processing of the sample.

The Irganox 1010 peak in the chromatogram from the extract of the 50kGy irradiated polymer was also shown to be pure using UV spectroscopy.

The two distorted peaks prominent in the chromatogram of the extract from the thermally treated sample were shown to be impure by comparison of the UV spectra on tracking across the peaks. The UV spectra across the peak eluting between 9 and 11 minutes are contained in figure 4.9. Judging from the UV spectra taken at longer retention times, some Irganox 1010 is present.

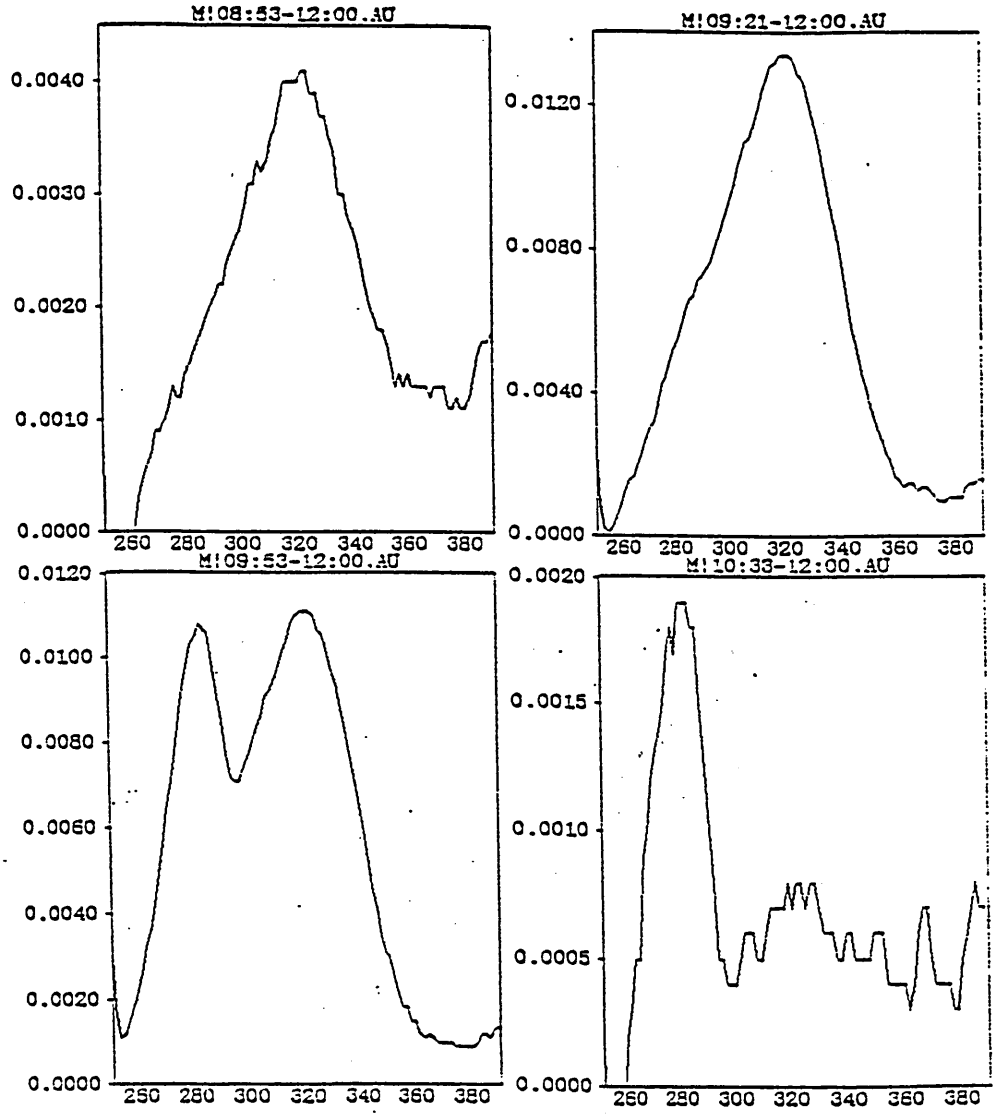
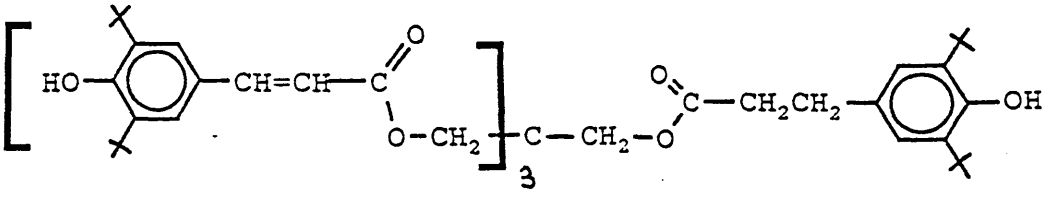


FIGURE 4.9 UV spectra taken at various intervals across the peak eluting between 9 and 11 minutes in the chromatogram of the extract from PP(H) 0kGy stabilized by Irganox 1010 after 400 hours at 150°C in air.

In order to further clarify the situation the extract from the thermally treated sample was analysed using the gradient hplc system detailed in section 2.8. The resulting chromatogram along with one for the extract from the untreated polymer is displayed in figure 4.10. This chromatogram shows that each of the peaks in question consists of three products. It is likely that each set of three compounds have very similar molecular masses or polarities since they appear very close to each other.

The UV spectra of the two components occuring just before Irganox 1010, and the first two components of the earlier set, have UV absorption maxima at longer wavelengths ($\lambda max \simeq 320nm$) This indicates the probable presence of cinnamate functionalities within their structures. A possible structure for such a compound is shown below. This is in stark contrast to the compounds produced upon irradiation.



In summary, the thermal treatment carried out in this case produces different transformation products to those produced by irradiation of samples containing Irganox 1010. The compounds produced by thermal treatment probably contain cinnamate functionalities. These results are similar to those obtained by Frank [2], reviewed in section 1.4.

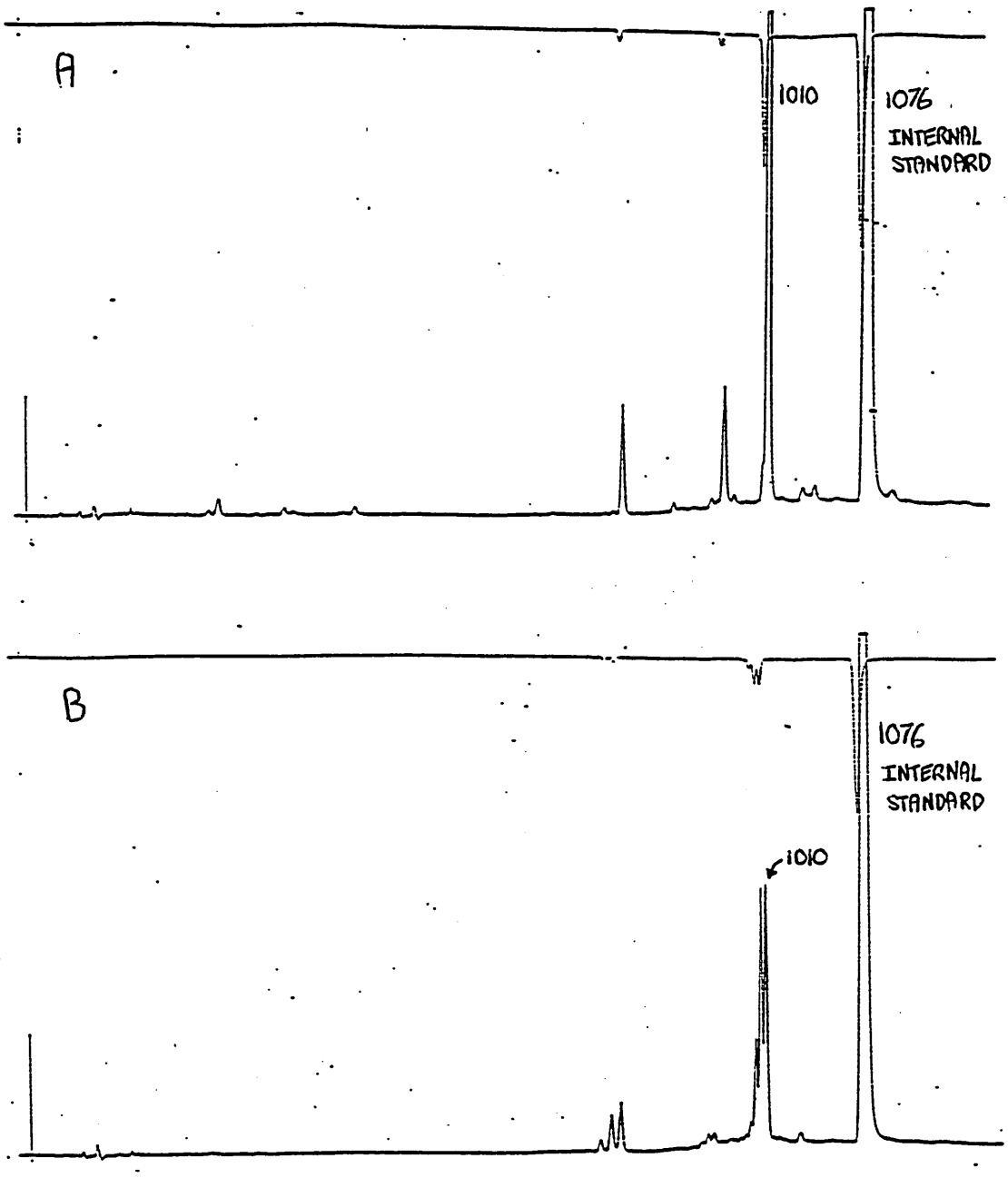


FIGURE 4.10 A) Gradient hplc chromatogram of the extract from 0kGy PP(H) containing 1010 - no thermal treatment
B) Gradient hplc chromatogram of the extract from 0kGy PP(H) containing 1010 - after 400 hours at 150°C

Two model reactions involving Irganox 1010 were also carried out.

The first of these involved oxidation using potassium hexacyanoferrate (III). This was carried out according to Duynstee's method.[3] It proved impossible to completely remove the solvent from the yellow product mixture which therefore remained a viscous liquid. A sample of the product mixture was dissolved in ethyl acetate and analysed using the isocratic hplc method detailed in section 2.8. The bulk of the product did not pass through the column. This was evidenced by the fact that the top of the guard column turned yellow. This would seem to provide further evidence for the polymeric structure suggested by Duynstee for this product (see section 1.4). This product is unlikely to be formed in stabilized polymers since the Irganox 1010 monomers are widely dispersed within the amorphous phase of the polymer.

However, a peak did appear on the chromatogram with a retention time similar to that of Irganox 1010. From the UV data (figure 4.11), this peak appeared to consist of unreacted Irganox 1010 at longer retention time and also a product with UV absorbance at longer wavelengths similar to that of the products of the thermal aging process. This product has yet to be identified but in view of its UV spectrum it probably contains cinnamate functionalities.

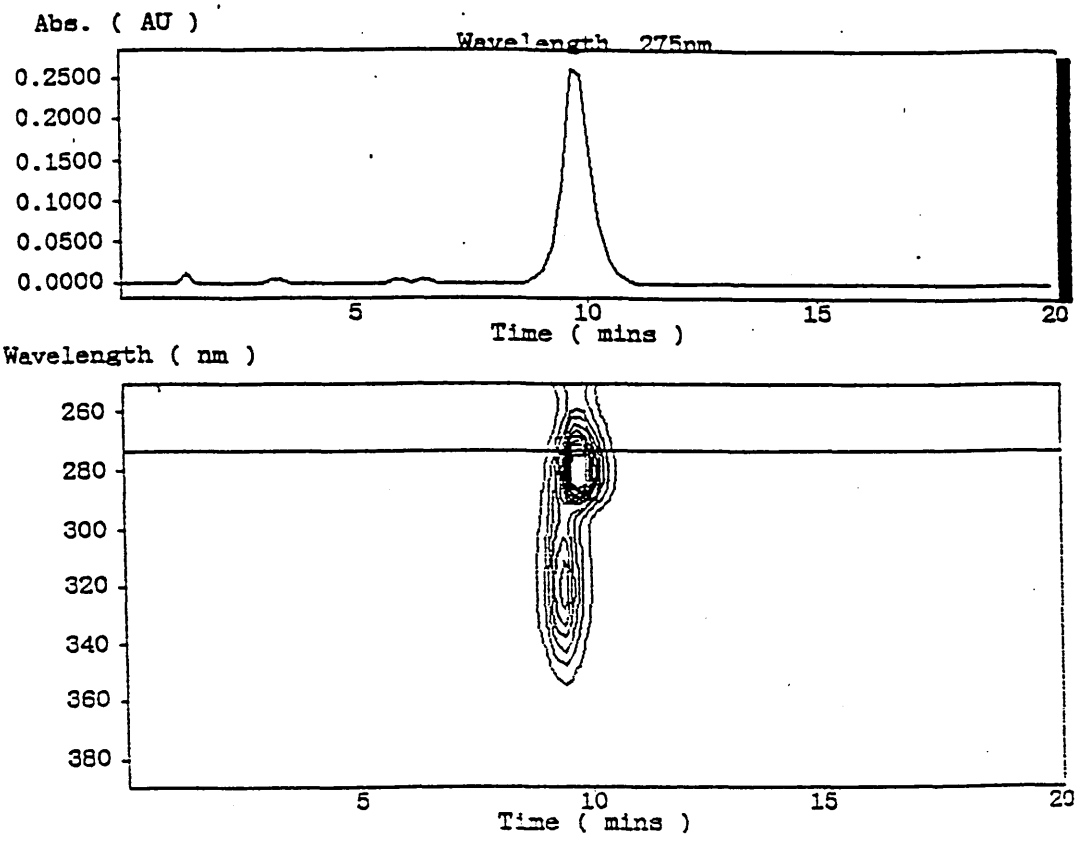


FIGURE 4.11 Isocratic hplc isochrom display for the product mixture obtained from the oxidation of Irganox 1010 using potassium hexacyanoferrate (III).

The second model reaction was that between Irganox 1010 and t-butylperoxyl radicals using the method detailed in section 2.13. The chromatogram of the resulting reaction mixture, analysed using the isocratic hplc technique detailed in section 2.8, is displayed in figure 4.12.

The chromatogram shows that at least seven Irganox 1010 transformation products are produced by this reaction. Some unreacted Irganox 1010 is also present (it has a retention time of about ten minutes). The UV spectra for six of the products with the greatest absorbance at 275nm are shown in figure 4.13. The products which elute at 3 minutes 19 seconds and 6 minutes 37 seconds appear to correspond to two of the compounds produced by irradiation on the basis of their retention times and UV spectra.

All six products appear to be phenolic in nature and do not appear to contain quinonoid or cinnamate functionalities.

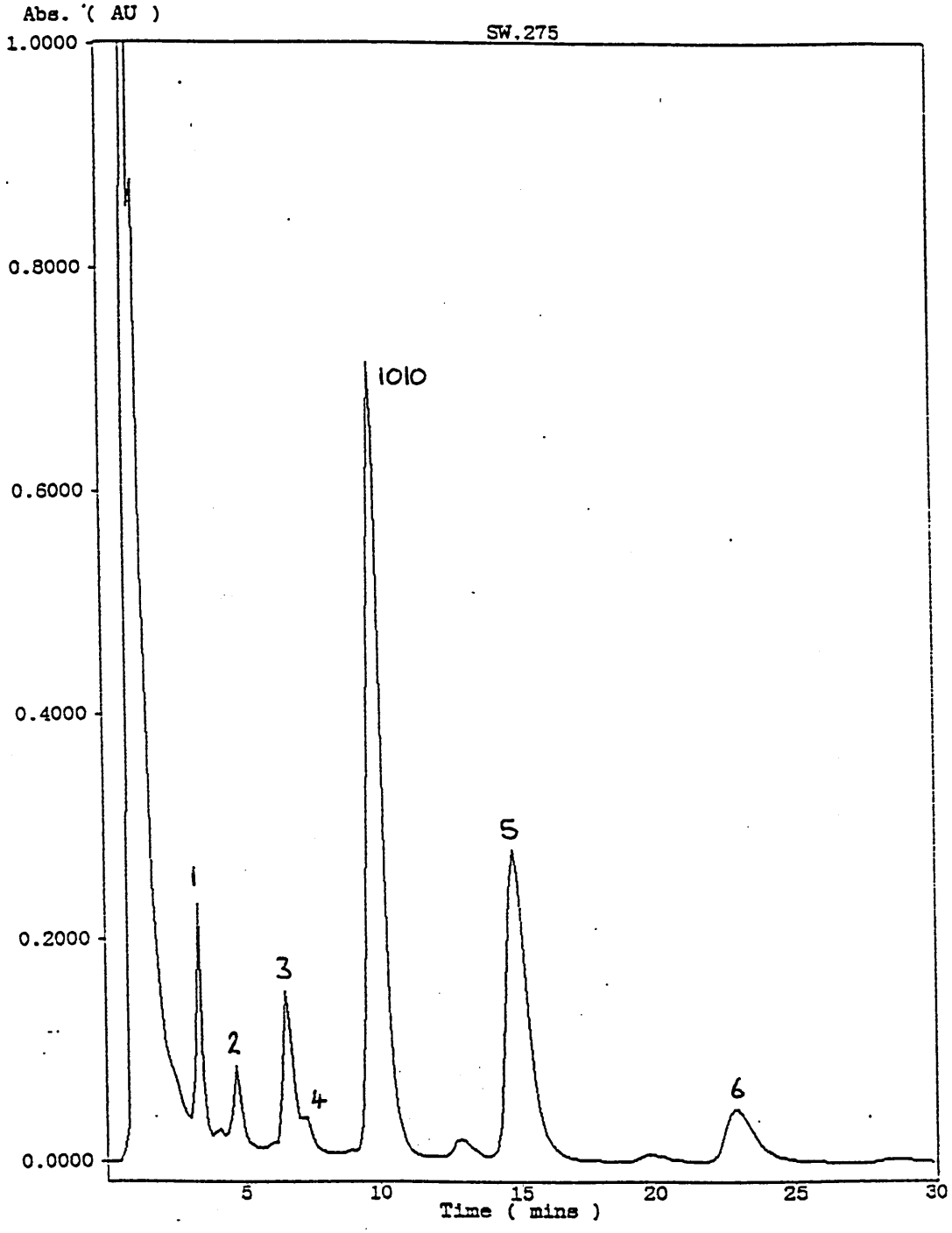


FIGURE 4.12 Isocratic hplc chromatogram for the product mixture from the reaction of Irganox 1010 with t-butylperoxyl radicals.

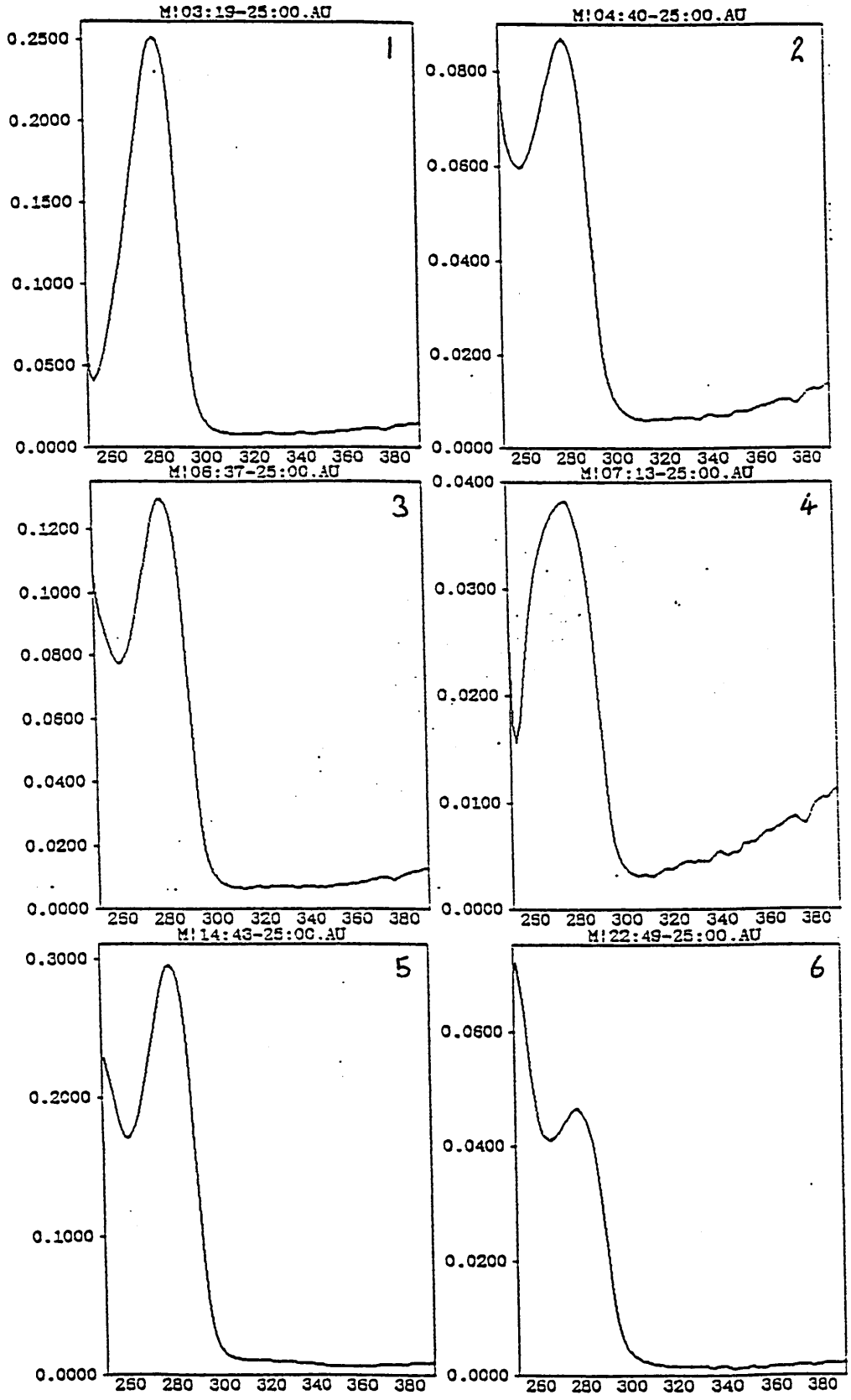


FIGURE 4.13 UV Spectra for the principal products of the reaction between Irganox 1010 and t-butylperoxyl radicals.

The reaction mixture was also analysed using the hplc-ms technique. The resulting TIC is contained in figure 4.14. The product at scan number 69 has a mass spectrum similar to that of 2,6-di-t-butylbenzoquinone. The mass spectra of the products at scan numbers 215 and 325 do appear to show molecular ions at 346 and 638 mass units respectively, but remain unidentified. The other three compounds all appear to have molecular masses above 1000 mass units (the mass limit of the spectrometer), suggesting that the 1010 framework is still largely intact.

Thus neither of these model reactions appear to be accurate representations of the processes occuring when Irganox 1010 in polypropylene is irradiated.

In conclusion, irradiation of polypropylene containing the antioxidant Irganox 1010 results in the production of many transformation products. A number of these products retain phenolic groups in their structures and do not contain cinnamate or quinonoid functionalities. This contrasts with the results obtained from thermally aging the stabilized polymers, which appears to produce cinnamates derived from Irganox 1010. The model reactions carried out using Irganox 1010 do not produce the same range of products as the reactions occurring in the stabilized polymer. Structures have been suggested for a number of the transformation products derived from Irganox 1010 under various conditions.

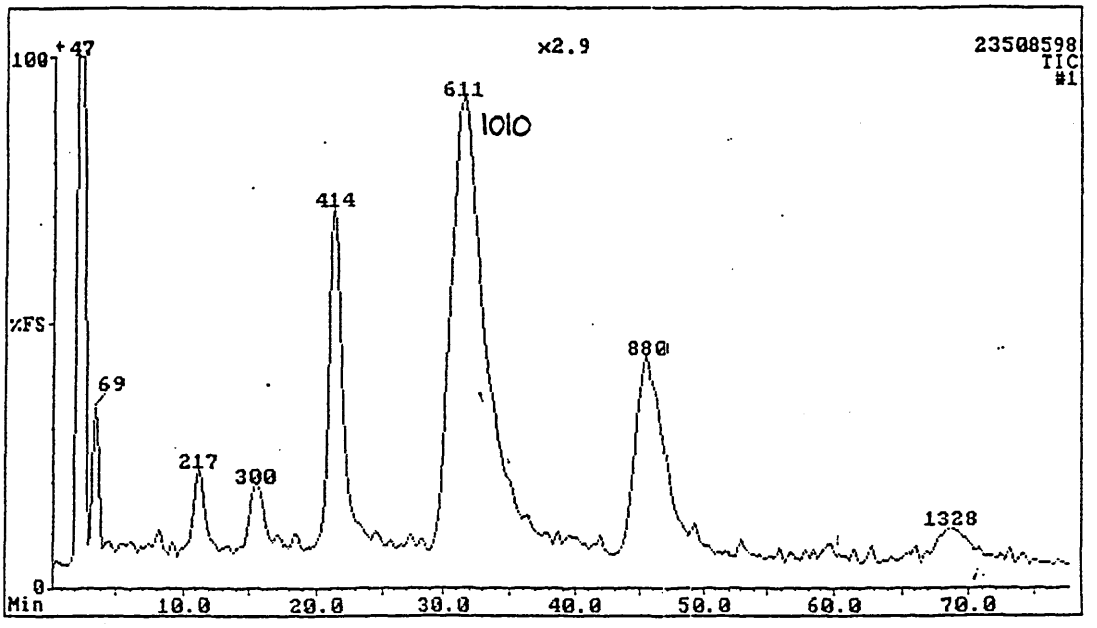


FIGURE 4.14 LC-MS TIC for the product mixture from the reaction of Irganox 1010 with t-butylperoxyl radicals.

4.3 TRANSFORMATION PRODUCTS OF IRGANOX 1076

The isocratic hplc chromatogram of the extract from polypropylene stabilized by Irganox 1076, subjected to an irradiation dose of 50kGy is presented in figure 4.15. At least four different transformation products are present in the extract and there are almost certainly other products which appear together at the solvent front, judging from the long wavelength absorption detected there.

The UV spectra of the four transformation products with the greatest absorbances at 275nm are shown in figure 4.16, together with that of Irganox 1076 itself. Component 1 shows some phenolic absorption and also some absorbance at longer wavelengths. Component 2 shows some conjugated double bond absorption and a small amount of absorbance above 300nm, possible indicating the presence of quinonoid units. Component 3 shows some phenolic absorbance and some absorption due to $\pi \rightarrow \pi^*$ transitions in the aromatic ring. Component 4 has a UV spectrum similar to that of Irganox 1076 with no absorption above 300nm indicating that it does not contain any quinonoid or cinnamate character and still contains the basic phenolic unit of Irganox 1076.

In addition there is a small amount of long wavelength absorbance characteristic of cinnamates towards the long retention time side of the Irganox 1076 peak. No components at longer retention times than this were detected using the isocratic hplc method.

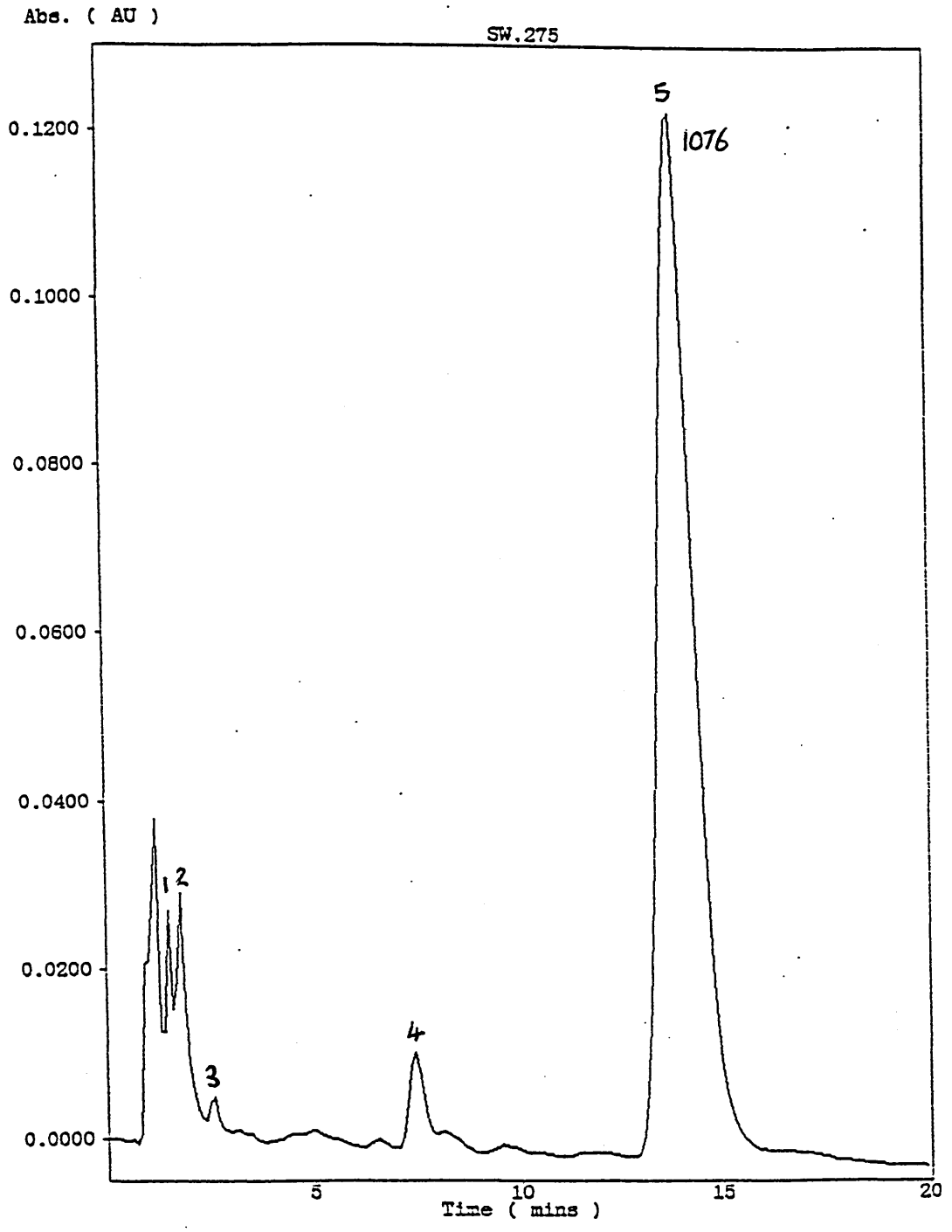


FIGURE 4.15 Isocratic hplc chromatogram of the extract from polypropylene homopolymer stabilized by Irganox 1076 subjected to an irradiation dose of 50kGy.

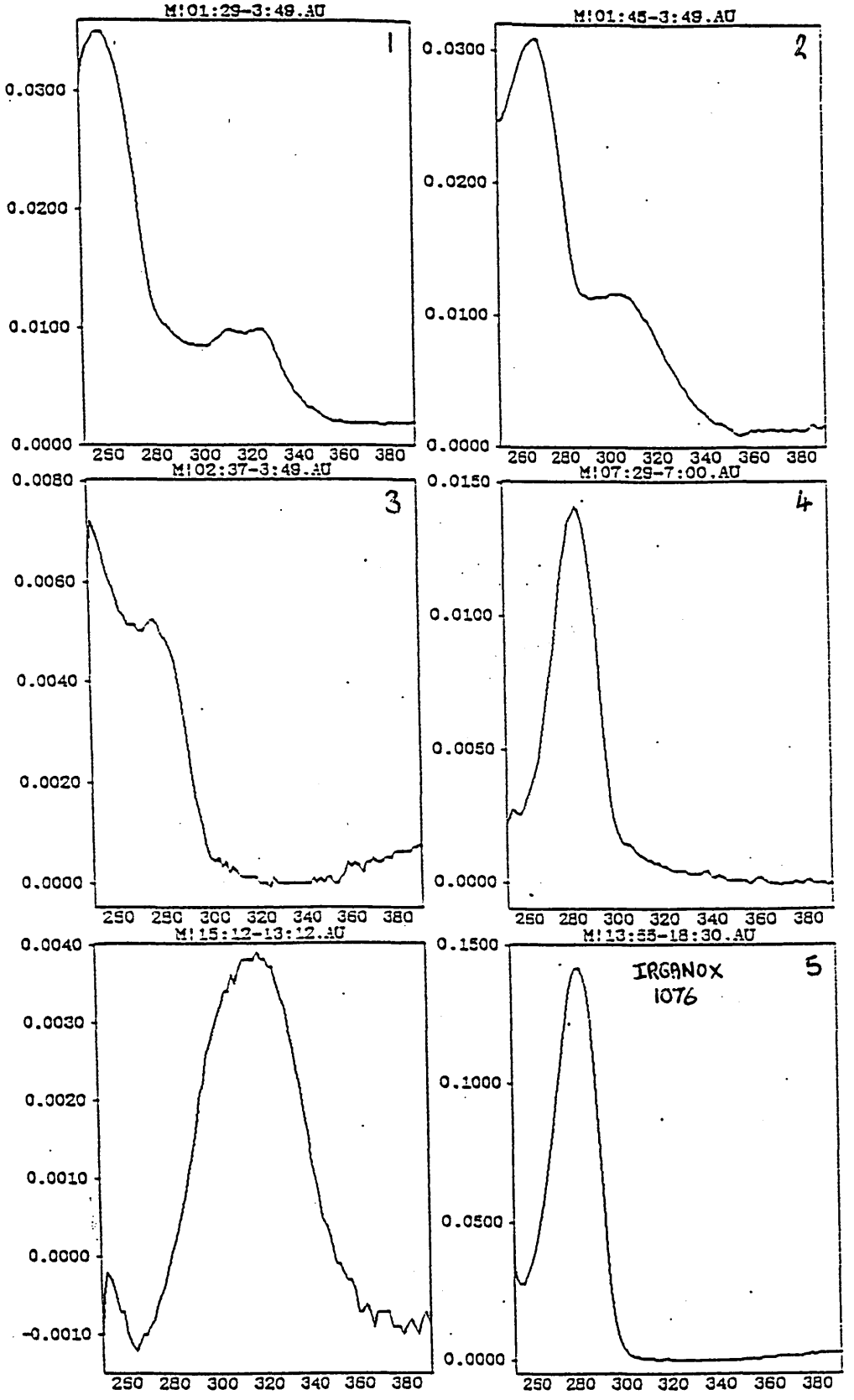


FIGURE 4.16 UV spectra of Irganox 1076 and its principal irradiation-derived transformation products

Gas chromatography - Mass spectrometry using the 5m long column (see section 2.7) revealed the presence of 2,6-di-t-butylbenzoquinone, which was identified by matching its spectrum with that contained in the spectral library. Another product of m/z = 276 was detected but not identified.

An hplc-ms investigation of this extract was carried out according to the method detailed in section 2.9. The resulting total ion chromatogram is displayed in figure 4.17.

A number of minor products were detected. However the peaks were not well resolved making it difficult to correlate the UV and mass spectral data. The mass spectra obtained for five of the products are shown in Figure 4.18.

The presence of these compounds and their molecular masses were highlighted using mass chromatograms. The product at scan number 261 appears to have a molecular mass of 570, 40 units greater than Irganox 1076, and remains unidentified. The product at scan number 290 appears to have a molecular mass of 410 and probably consists of two linked aromatic rings, each possessing two t-butyl groups. However, the precise structure of this compound has yet to be elucidated. The product at scan number 390 corresponds to component 4 in the isocratic hplc chromatogram, and has a mass of 474. Consistent with this, and its UV spectrum, the following structure is suggested :

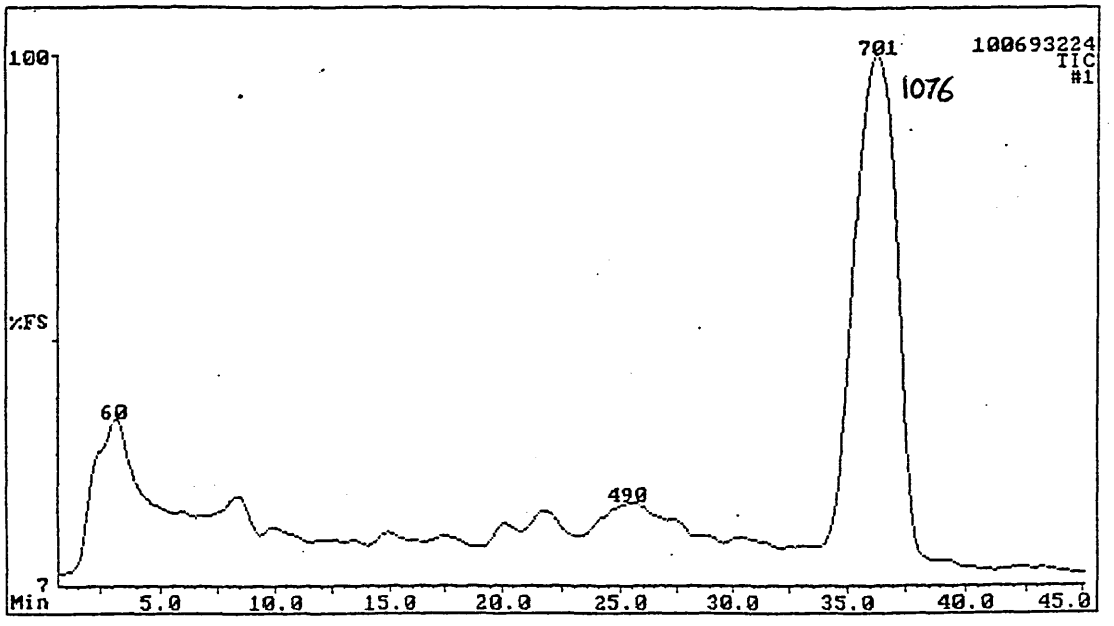


FIGURE 4.17 LC-MS TIC of the extract from polypropylene homopolymer stabilized by Irganox 1076, subjected to an irradiation dose of 50kGy.

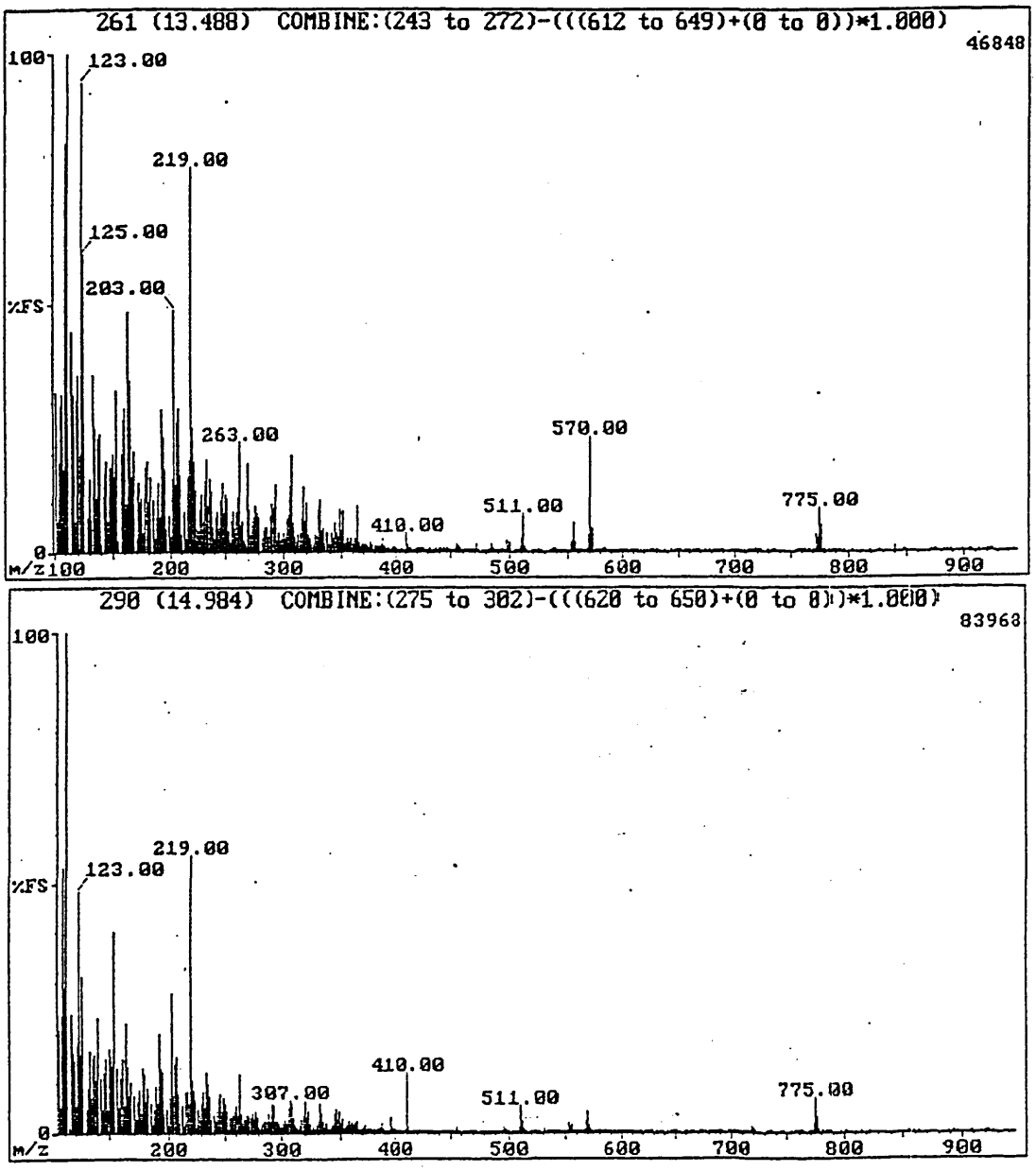
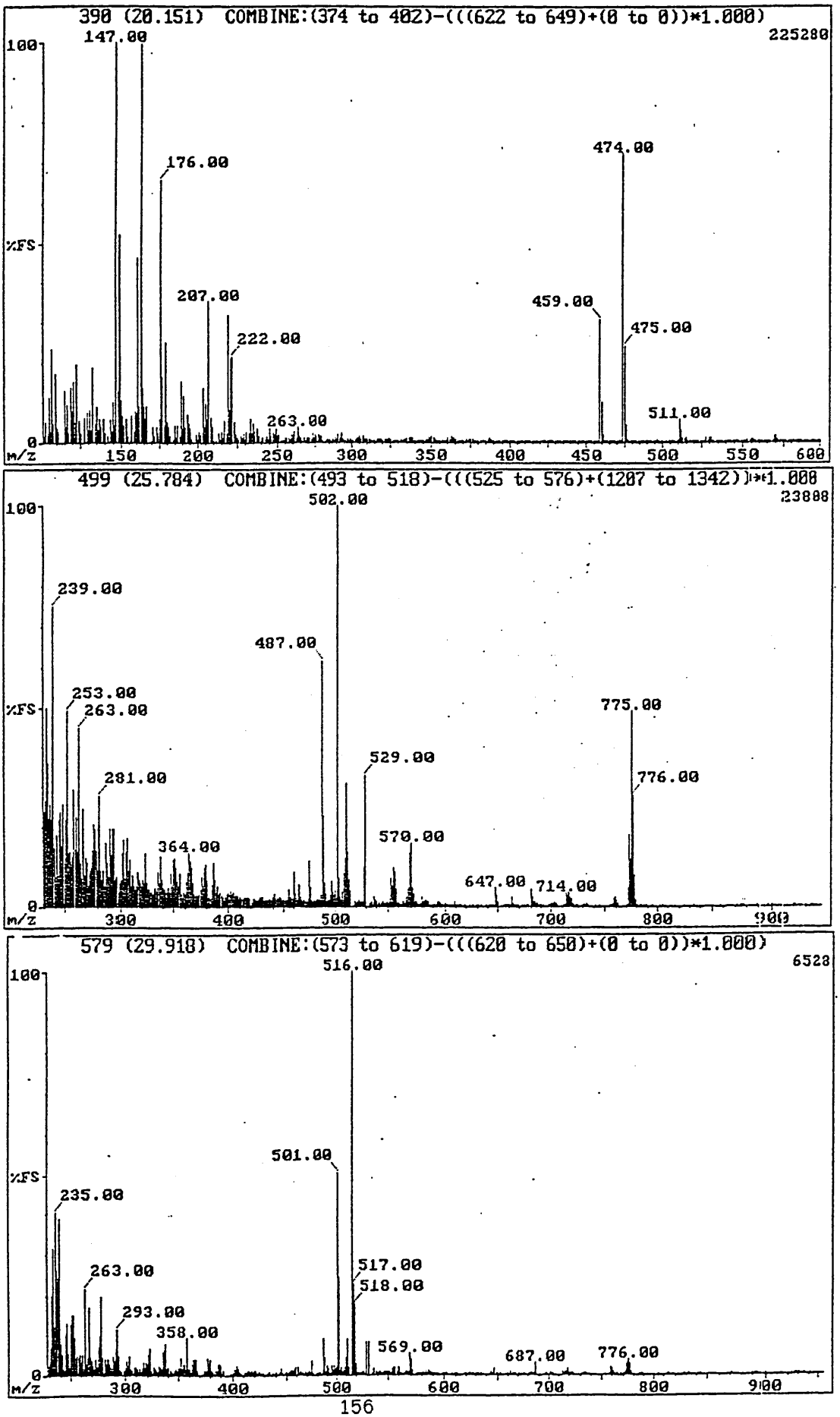
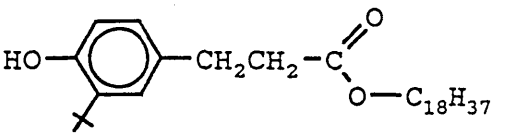


FIGURE 4.18 (A) Mass spectra obtained for some of the irradiation-derived transformation products of Irganox 1076.

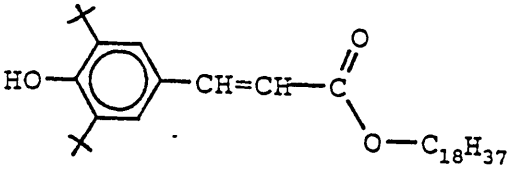
FIGURE 4.18 (B)


390 (20.151) COMBINE:(374 to 402)-(((622 to 649)+(0 to 0))*1.000)
225280
147.00
176.00
474.00
207.00
459.00
475.00
222.00
263.00
511.00
%FS
m/z
499 (25.784) COMBINE:(493 to 518)-(((525 to 576)+(1207 to 1342))*1.000
23888
502.00
239.00
487.00
253.00
263.00
775.00
529.00
281.00
776.00
364.00
570.00
647.00
714.00
579 (29.918) COMBINE:(573 to 619)-(((620 to 650)+(0 to 0))*1.000)
6528
516.00
501.00
235.00
263.00
517.00
518.00
293.00
358.00
569.00
687.00
776.00



This compound is obviously produced by the loss of a neutral molecule of 56 mass units i.e. the loss of 2-methylpropene from the parent antioxidant.

A structure has also yet to be suggested for the product at scan number 499 which has an apparent molecular mass of 529. The product at scan number 579 appears to have a mass of 516 which suggests the loss of a $-CH_2-$ group from Irganox 1076. This unit could be lost from the hydrocarbon chain or from one of the t-butyl groups. However, a definitive structure has yet to be proposed. The minor product appearing at a slightly longer retention time than Irganox 1076 was detected using a mass chromatogram and showed an apparent molecular ion at 528 mass units. It was suggested that this product was the cinnamate shown below and this was supported by later studies.



Using the gradient hplc system detailed in section 2.8, reveals that, as with Irganox 1010 the situation is much more complex and there are many other minor transformation products formed which have shorter retention times than Irganox 1076.

In addition to these, it revealed the presence of a number of products appearing at longer retention times than Irganox 1076 which were not detected on the usual isocratic system. The products are probably various dimeric molcules which are known to be formed upon the oxidation of Irganox 1076.[3-5] The chromatogram at 275nm produced using the gradient system is presented in figure 4.19.

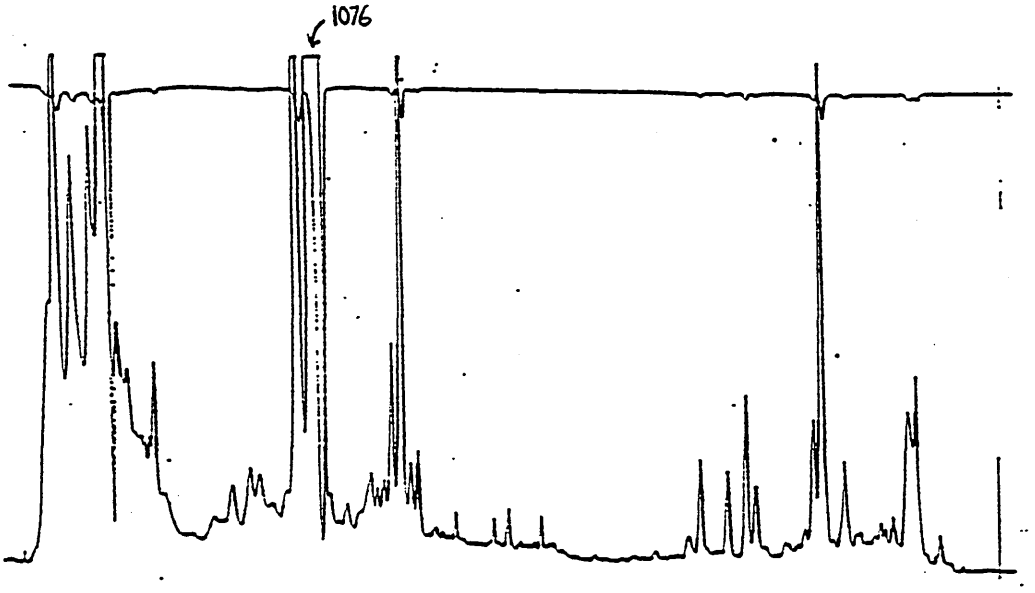


FIGURE 4.19 Gradient hplc chromatogram of the extract from polypropylene homopolymer stabilized by Irganox 1076, subjected to an irradiation dose of 50kGy.

In order to further investigate the production of these dimers, an isocratic mobile phase consisting of ethyl acetate:methanol:water 50:38:10 v/v was used.

Irganox 1076 was oxidised using potassium hexacyanoferrate (III) as described by Duynstee [3] and also using silver monoxide as described by Lerchóva et al.[6] Both these conditions were found to produce the same five compounds, though not in the same proportions. The 3D plot obtained from chromatographing the product mixture produced by the first of these procedures is contained in figure 4.20 and the UV spectra of the products are displayed in figure 4.21.

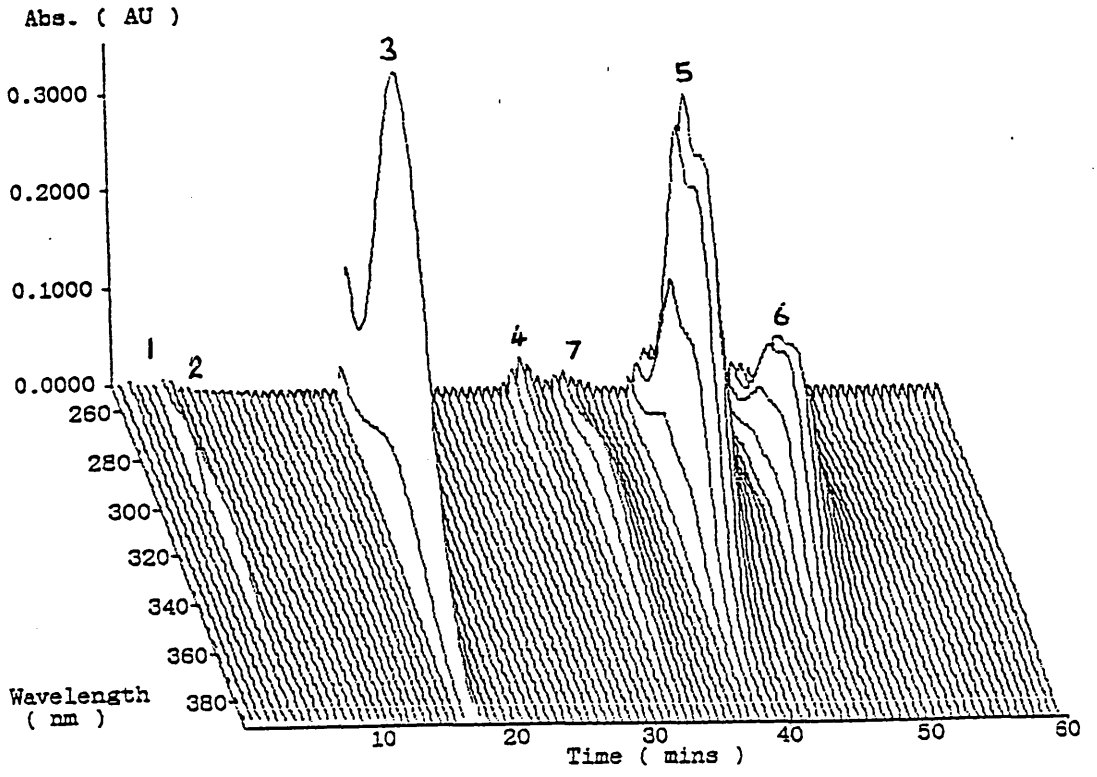


FIGURE 4.20 Isocratic hplc three dimensional plot of wavelength, against time, against absorbance, for the reaction mixture from the oxidation of Irganox 1076 using potassium hexacyanoferrate (III).

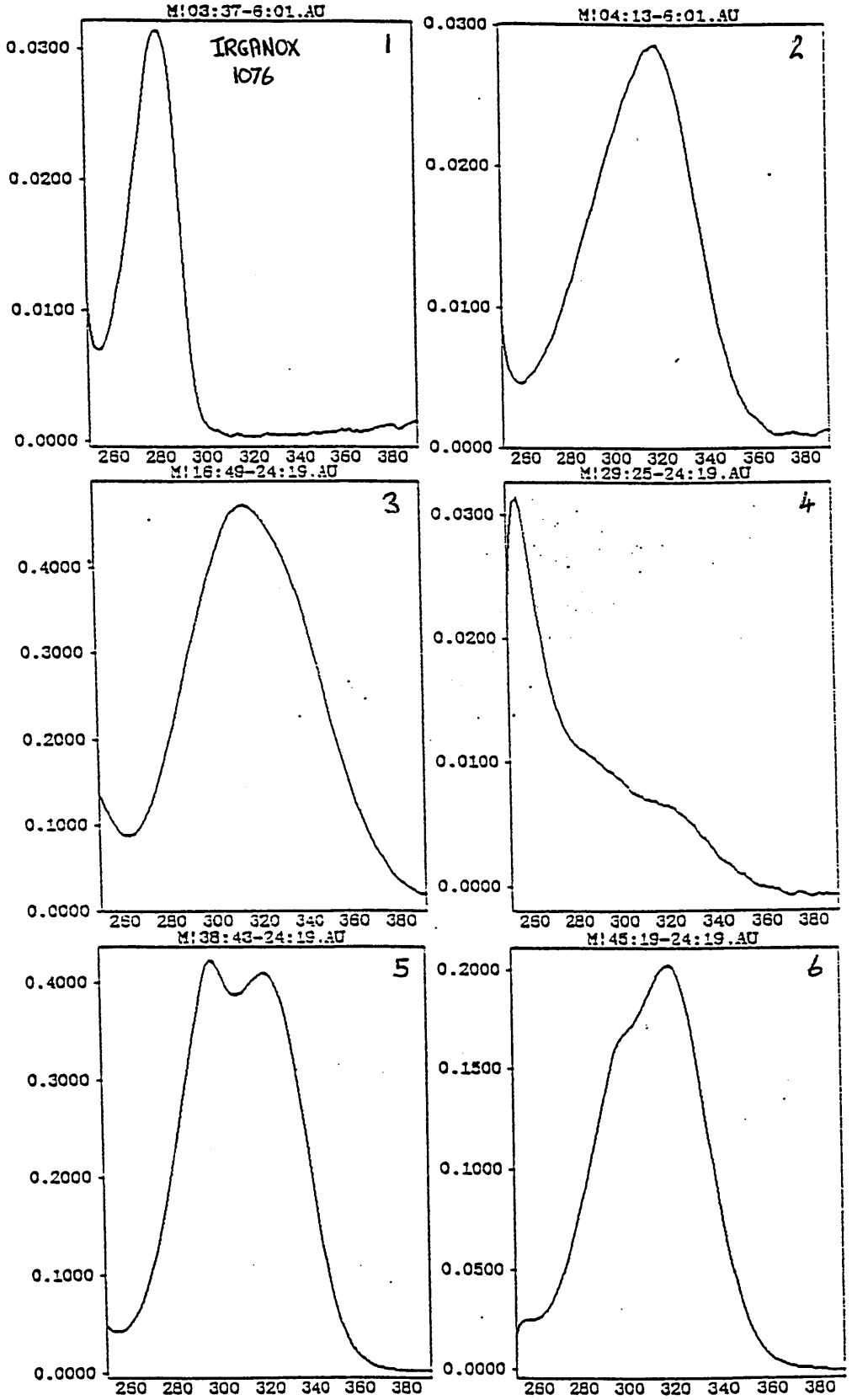


FIGURE 4.21 UV spectra of Irganox 1076 and its oxidation products produced using potassium hexacyanoferrate (III).

This work was compared with that carried out by Jonas et al [4] who have presented structures and UV data for this type of compound.

From this comparison it was deduced that:

i) component 1 is the unreacted Irganox 1076

ii) component 2 is the cinnamate of Irganox 1076
- structure A.

iii) component 3 is the biscinnamate based on Irganox 1076
- structure B

iv) component 4 is the phenol/quinone dimer
- structure C

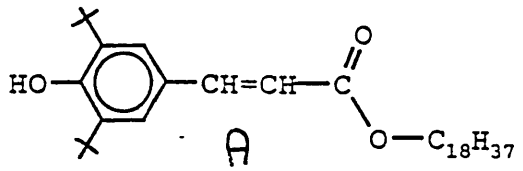
v) component 5 is the dl-diastereomer of the unconjugated bisquinonemethide of Irganox 1076
- structure D

vi) component 6 is the meso-diastereomer of the unconjugated bisquinonemethide of Irganox 1076
- structure D.

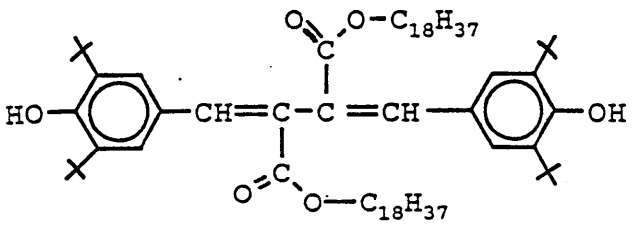
vii) The conjugated bisquinonemethide, structure E does not appear to be produced by these methods.

Component 7 remains unidentified and the identity of all these compounds has yet to be confirmed by fraction-collecting followed by ^{1}H nmr spectroscopy of the products and DIP-MS analysis.

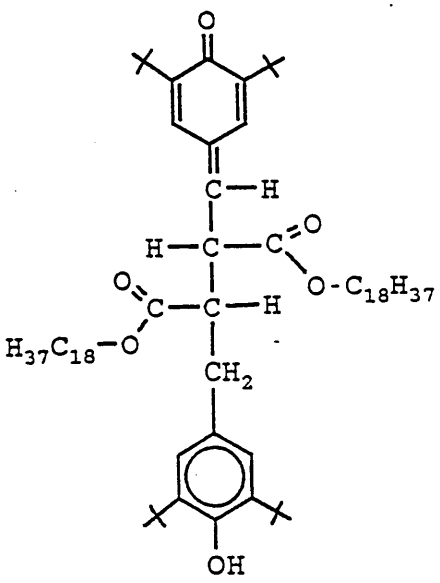
STRUCTURES A - E



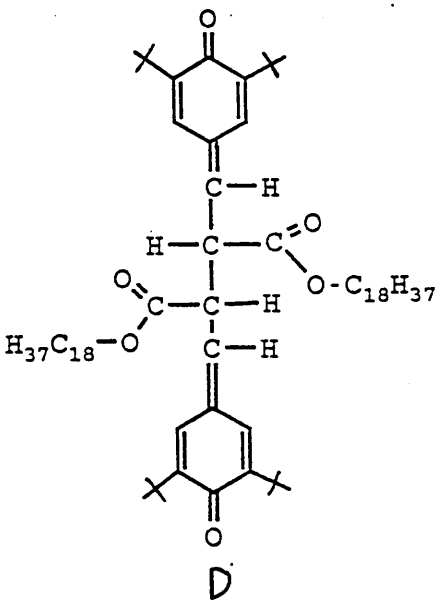
A



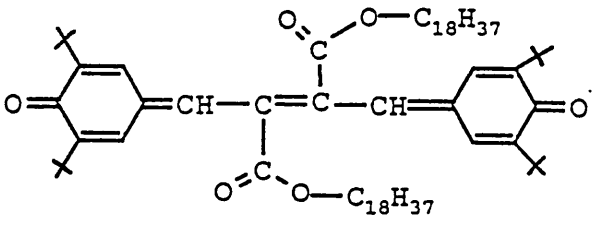
B



C



D



E

The extract from polypropylene stabilized by Irganox 1076, after 50kGy, was analysed using the modified hplc mobile phase and found to contain the biscinnamate (B). The gradient hplc chromatogram suggests that very low levels of the other compounds may also be present.

A sample of polypropylene stabilized by Irganox 1076 was subjected to the thermal aging process detailed in section 2.12.

The resulting isocratic hplc chromatogram produced using the method detailed in section 2.8, is displayed in figure 4.22. Similar chromatograms from extracts produced for the same polymer before either irradiation or thermal treatment and after an irradiation dose of 50kGy are also displayed in figure 4.22 for comparison. Irganox 1010 is present in chromatograms A and B as an internal standard.

The untreated polymer chromatogram clearly shows the peak due to Irganox 1076 but is otherwise almost clear of other compounds. The thermally treated sample appears to contain three transformation products, the one appearing just after Irganox 1076 being the most prominant. This product also appears to be present in the irradiated sample, but at a much lower level. The UV spectra for the three products from thermal treatment are shown in figure 4.23.

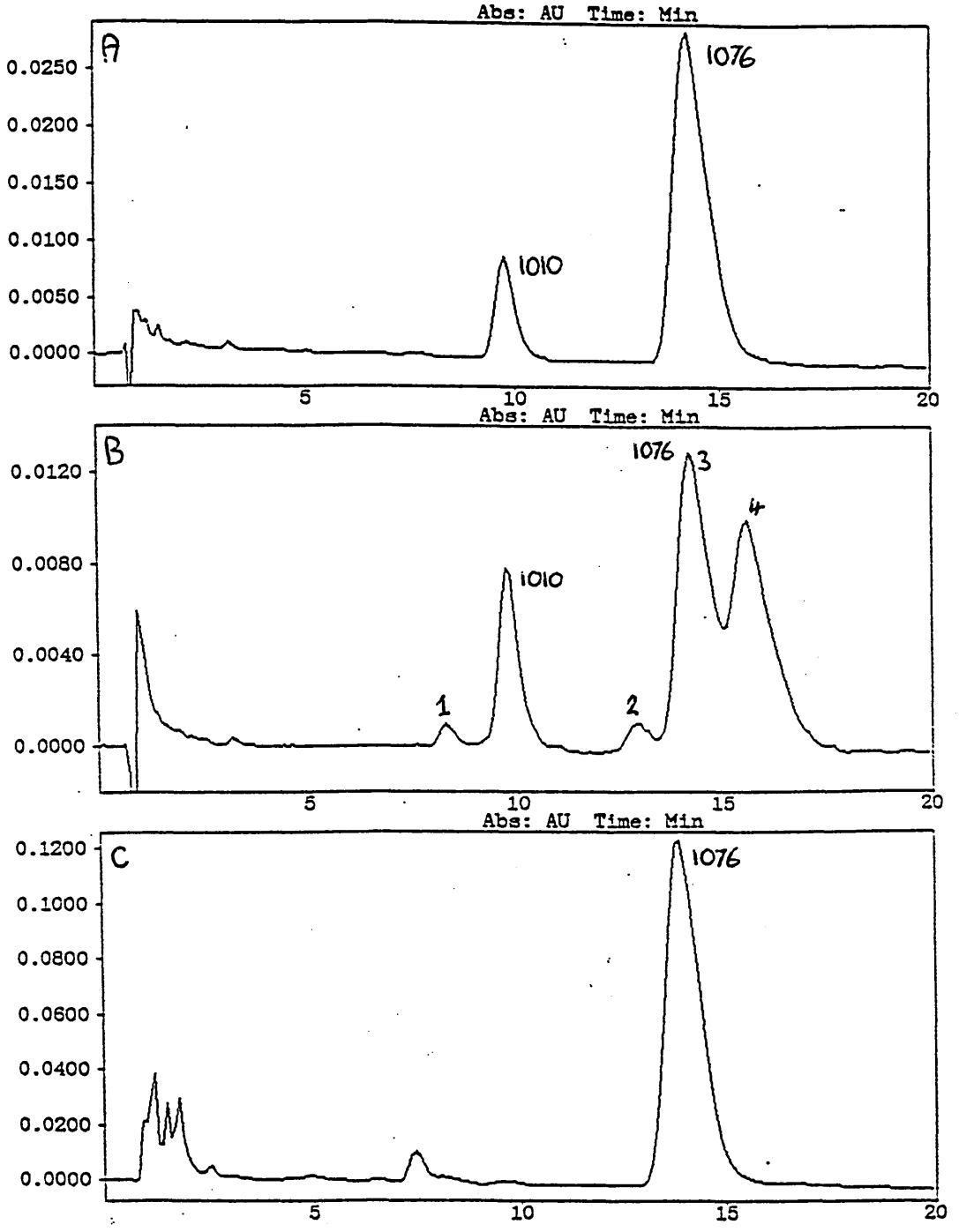


FIGURE 4.22 A) Hplc chromatogram of the extract from 0kGy PP(H) containing 1076
-no thermal treatment
B) Hplc chromatogram of the extract from 0kGy PP(H) containing 1076
- after 279 hours at 150°C in air
C) Hplc chromatogram of the extract from 50kGy PP(H) containing 1076
- no thermal treatment

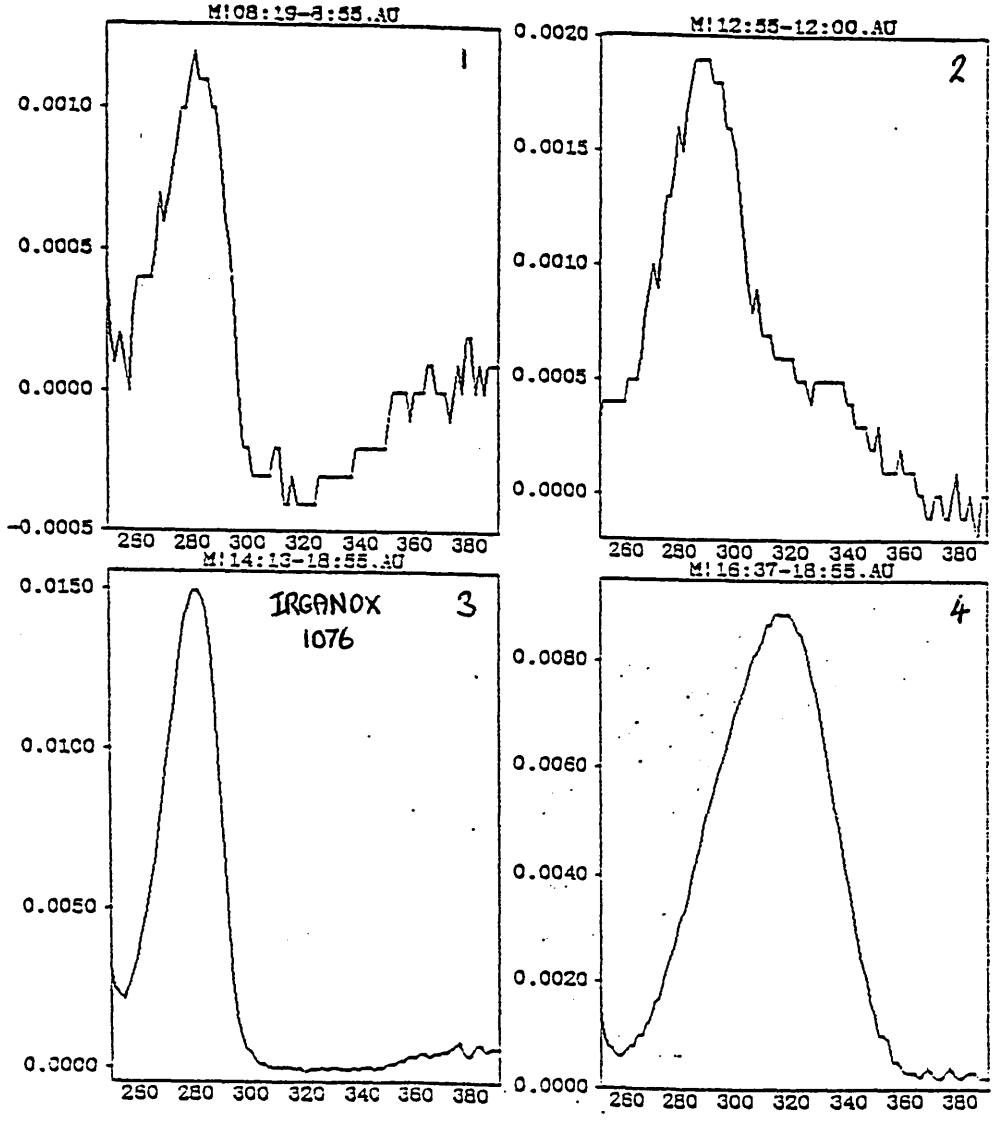


FIGURE 4.23 UV spectra of Irganox 1076 and its principal thermal transformation products.

The product appearing after Irganox 1076 has an intense UV absorption at about 320nm, which would suggest that it has cinnamate character. The work by Jonas et al [4] would also seem to suggest that this compound is the cinnamate (A) derived from Irganox 1076. The other two products do not appear to absorb at wavelengths longer than 300nm which indicates that they have retained the basic saturated aromatic character of Irganox 1076.

In order to determine whether the product appearing just after Irganox 1076 was in fact the related cinnamate (A), the authentic material was obtained [7], and characterised using the isocratic hplc system. Its retention time and UV spectrum were found to be almost identical with those of the transformation product. The authentic sample was analysed by both DIP-MS and LC-MS and found to have the expected relative molecular mass of 528. Its structure was confirmed using ^{1}H nmr spectroscopy. The ^{1}H nmr spectra and their interpretations for Irganox 1076 and its related cinnamate are shown in figure 4.24. It is important to note that although the quinone methide derived from Irganox 1076 would also have a relative molecular mass of 528 its ^{1}H nmr spectrum would be different to that of the cinnamate.

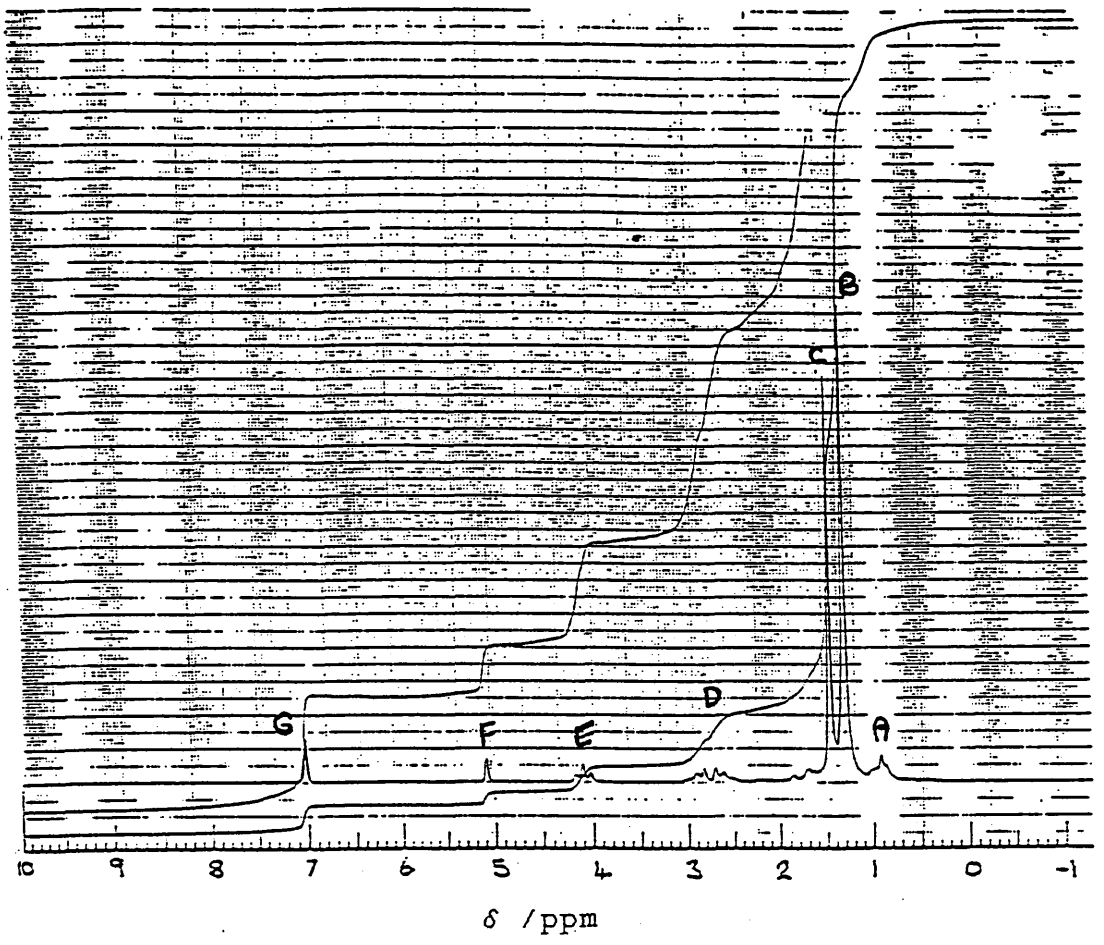
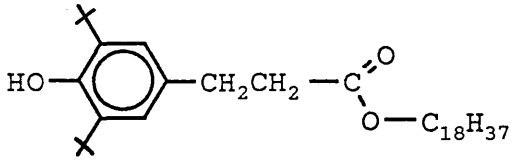


FIGURE 4.24 (A) ^1H nmr spectrum of authentic Irganox 1076



A ≡ -COOR-CH_3

B ≡ -$COOCH_2CH_2C_{15}H_{30}CH_3$

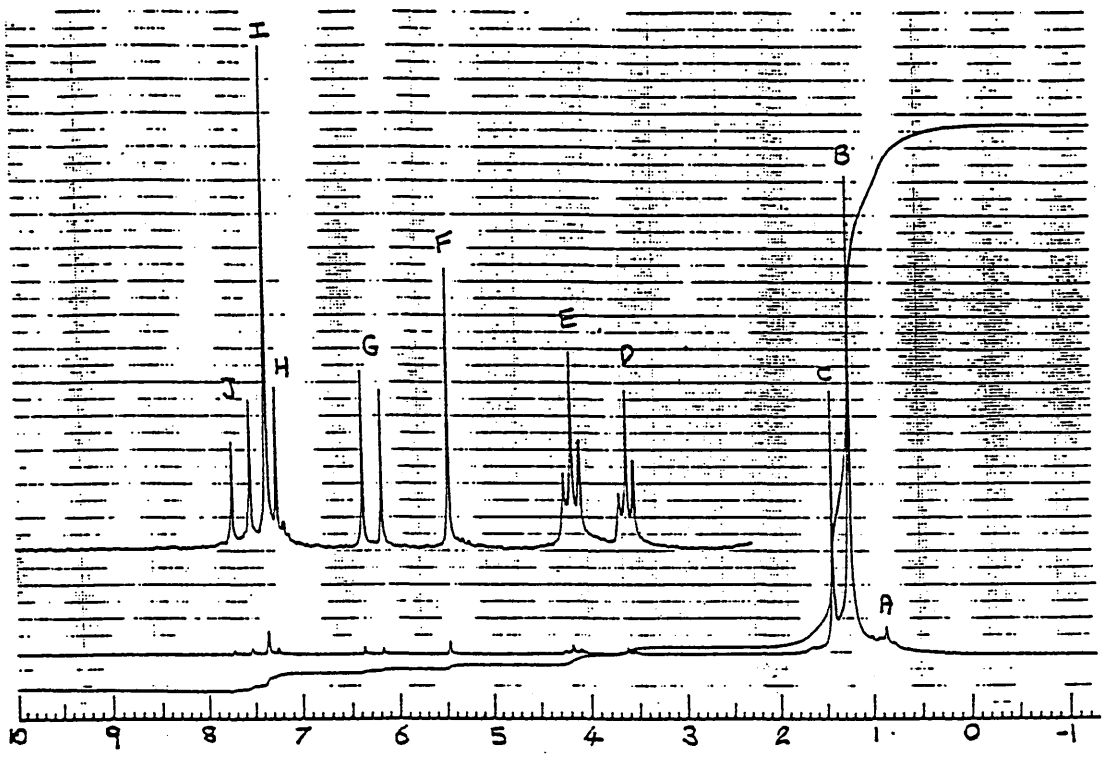
C ≡ -C_4H_9

D ≡ -Ar-CH_2CH_2-COOR

E ≡ -$COOCH_2CH_2$R

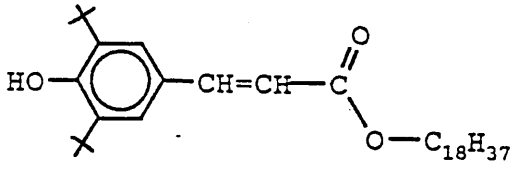
F ≡ -Ar-OH

G ≡ -Ar-H



δ /ppm

FIGURE 4.24 (B) ^{1}H nmr spectrum of the authenic sample of the cinnamate derived from Irganox 1076



A ≡ $-COOR-CH_3$

B ≡ $-COOCH_2CH_2C_{15}H_{30}CH_3$

C ≡ $-C_4H_9$

D ≡ $-COOCH_2CH_2R$

E ≡ $-COOCH_2CH_2R$

F ≡ -Ar-OH

G ≡ -Ar-CH=CH-COOR

H ≡ $CHCl_3$ in $CDCl_3$

I ≡ -Ar-H

J ≡ -Ar-CH=CH-COOR

The extract from the thermally treated sample was also analysed using the lc-ms technique detailed in section 2.9. The resulting total ion chromatogram is displayed in figure 4.25.

In this case there appears to be an increased noise level which makes good mass spectra difficult to obtain. However, mass spectra for the products at scan numbers 415 and 509 are displayed in figure 4.26. These products appear to have molecular masses of 544 and 542 respectively. The identity of these two compounds is still uncertain but, the former may be of a phenolic type and be converted to a cinnamate or quinonoid structure with the loss of two mass units to give the latter product. The mass spectra for Irganox 1076 and the product at scan number 747 are also displayed in figure 4.26. The mass spectrum for the product at scan number 747 is identical to that of the synthetic cinnamate. There are other very minor products but this extract does not appear to contain the products with relative molecular masses of 474, 570, 529 and 516 which are found in the extract from the irradiated polymer containing Irganox 1076.

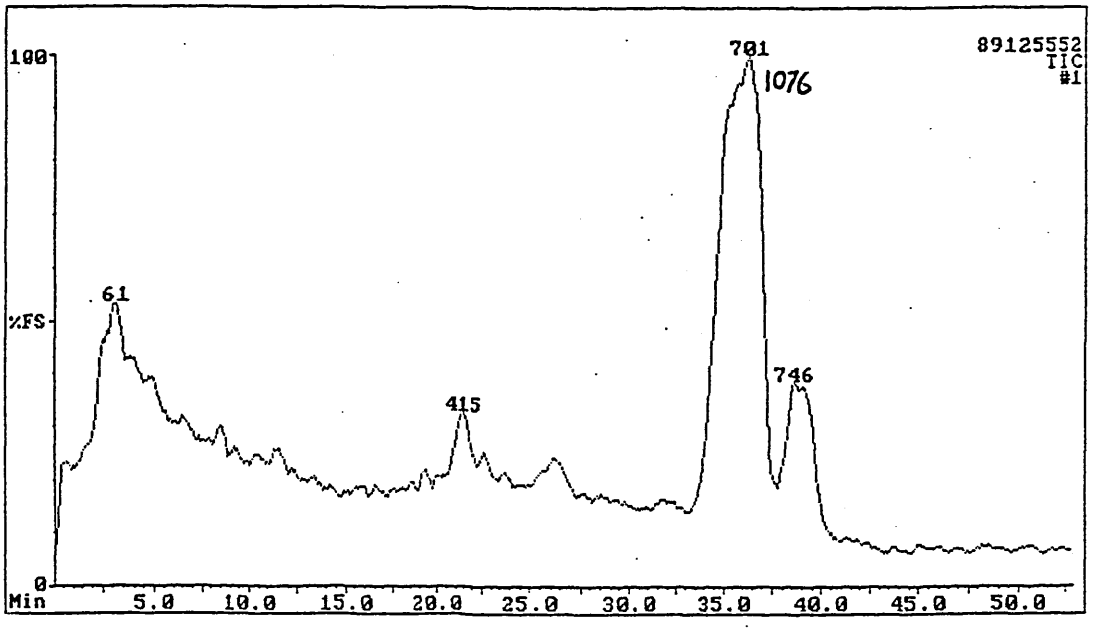


FIGURE 4.25 LC-MS TIC for the extract from polypropylene homopolymer stabilized by Irganox 1076 after thermal aging for 279 hours at 150°C in air.

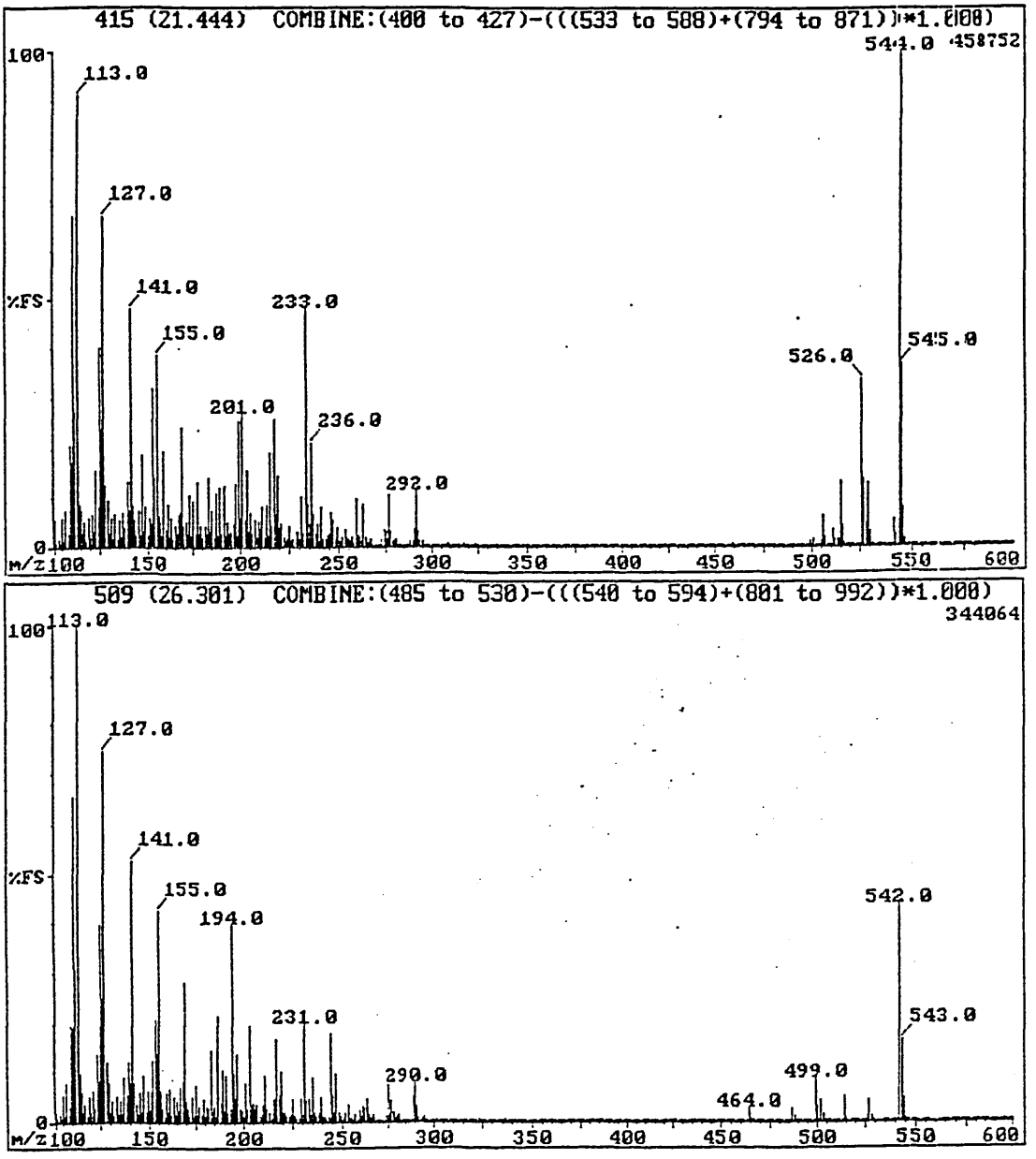


FIGURE 4.26 (A) Mass spectra of two thermal transformation products of Irganox 1076.

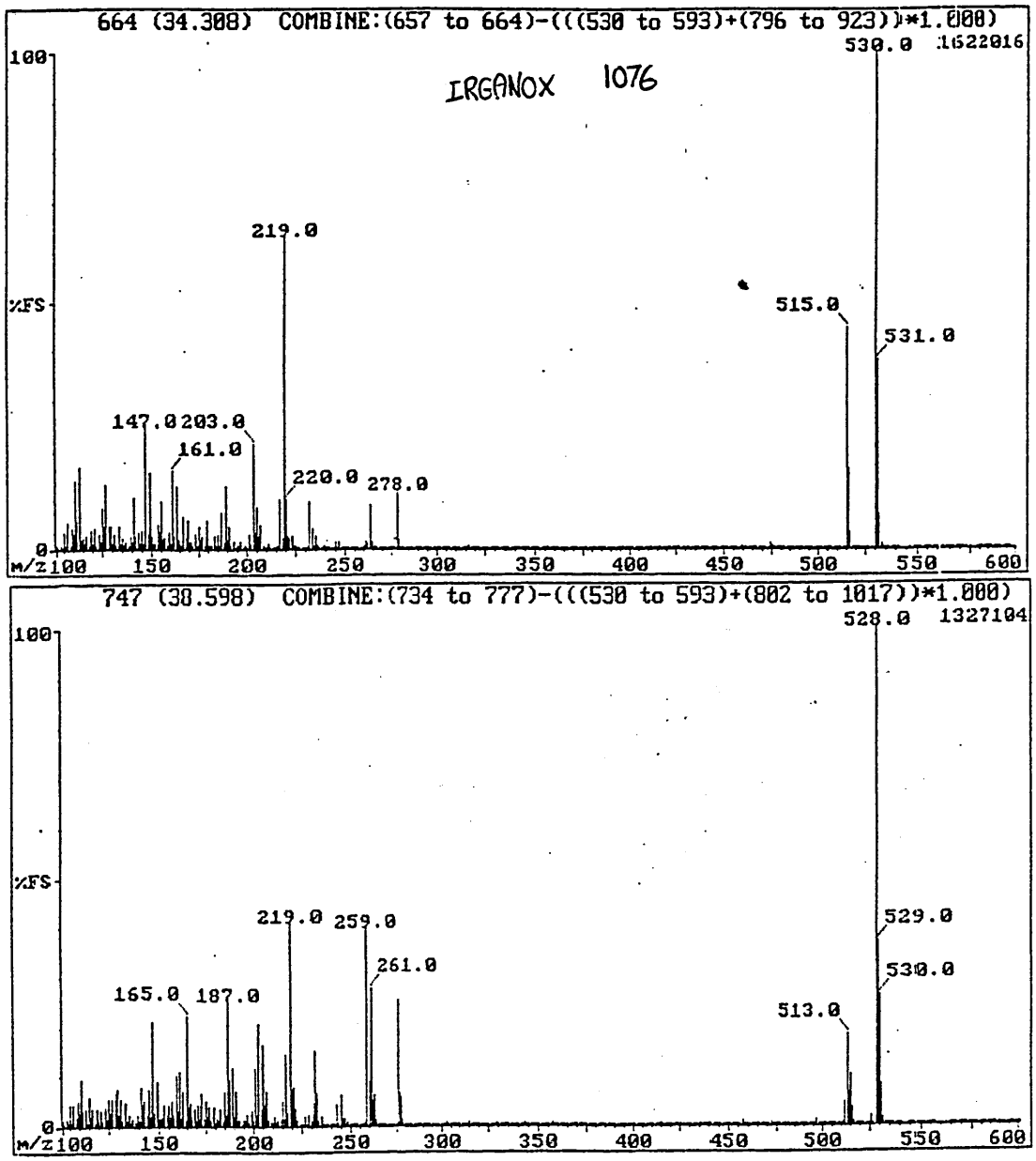


FIGURE 4.26 (B) Mass spectra of Irganox 1076 and its related cinnamate.

The possibility that the thermal treatment results in the production of the 'dimeric' compounds derived from Irganox 1076 was also investigated using the modified isocratic hplc mobile phase. Using this method the biscinnamate was detected, but none of the other 'dimers'.

Because of the low levels of many of these transformation products it is difficult to identify them and compare the two processes accurately; however, there do appear to be differences between the two processes.

A model reaction between Irganox 1076 and t-butylperoxyl radicals was also carried out according to the method detailed in section 2.13. The resulting isochrom display is shown in figure 4.27. This shows the presence of two major and two minor products from this reaction. The UV spectra of these compounds are shown in figure 4.28. None of these products appear to correspond to those produced by irradiation.

The reaction mixture was also analysed using LC-MS. The resulting total ion chromatogram is displayed in figure 4.29. The two minor products observed using the UV detector were not apparent using this technique. The peak at scan number 692 is due to Irganox 1076. The other three peaks at scan numbers 175, 422 and 1120 give rise to the mass spectra shown in figure 4.30.

The product at scan number 175 appears to have a molecular mass of 647. However, the molecular mass of the other compounds remains in doubt, and it seems likely that they have masses above the mass limit of the VG Trio-1 mass spectrometer.

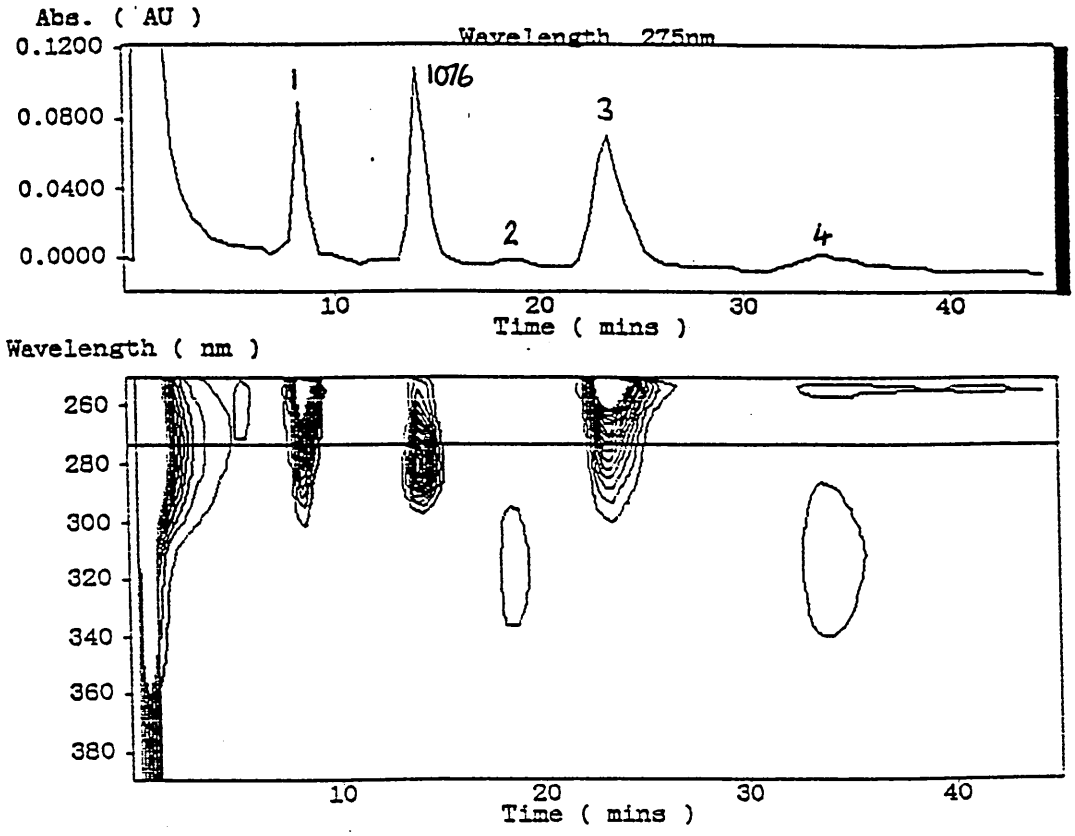


FIGURE 4.27 Isocratic isochrom display obtained for the product mixture of the reaction between Irganox 1076 and t-butylperoxyl radicals.

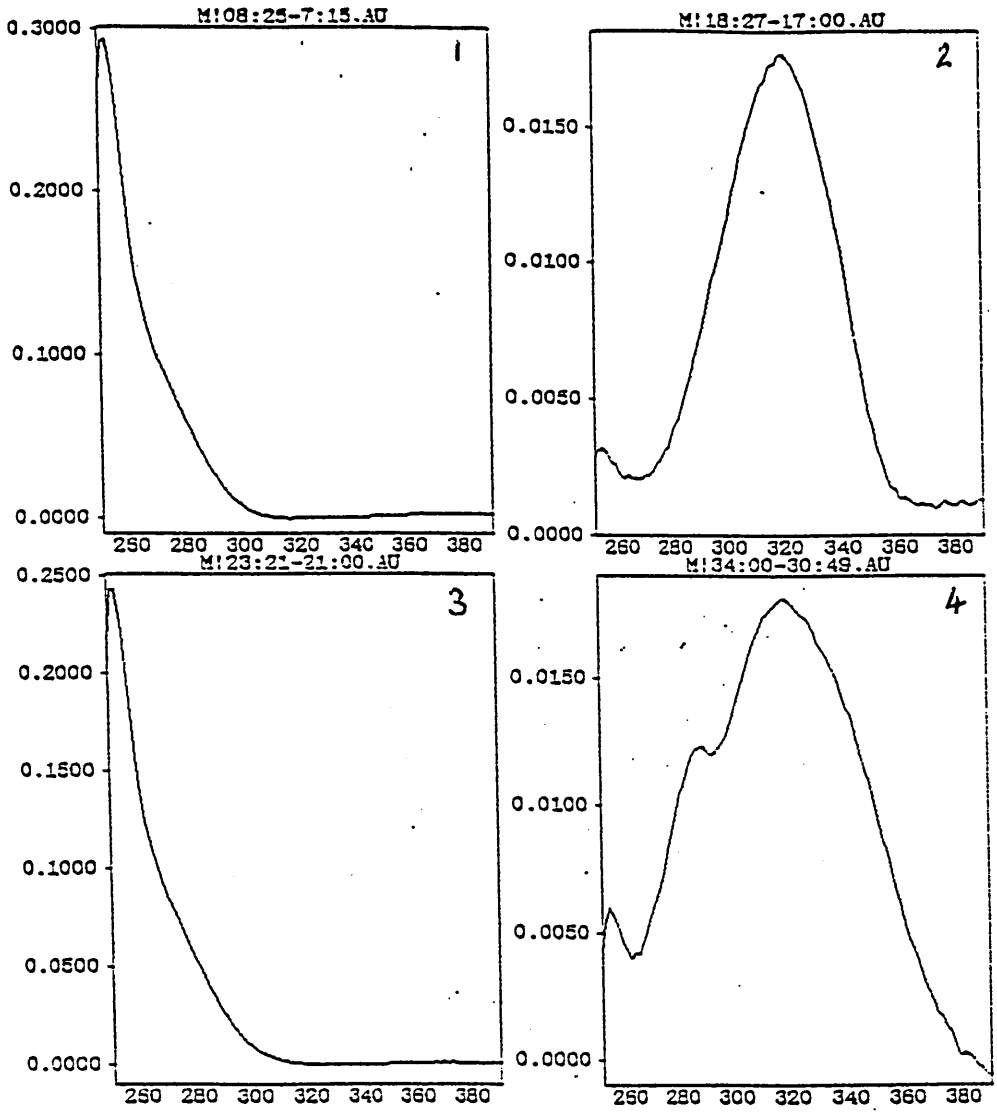


FIGURE 4.28 UV spectra of four of the products from the reaction between Irganox 1076 and t-butylperoxyl radicals.

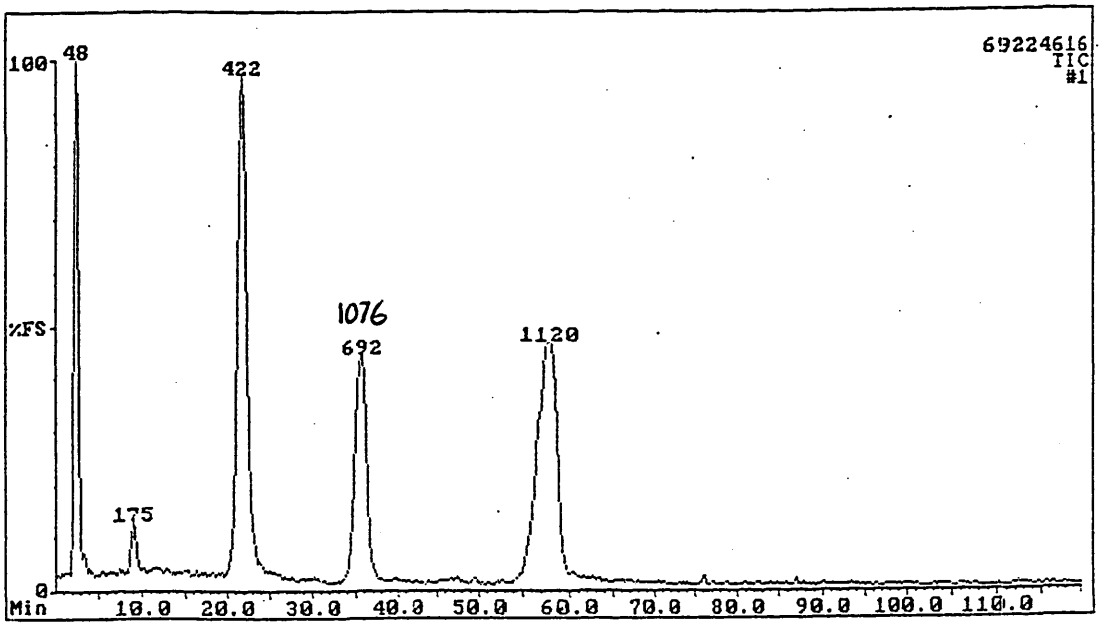


FIGURE 4.29 LC-MS TIC for the product mixture from the reaction between Irganox 1076 and t-butylperoxyl radicals.

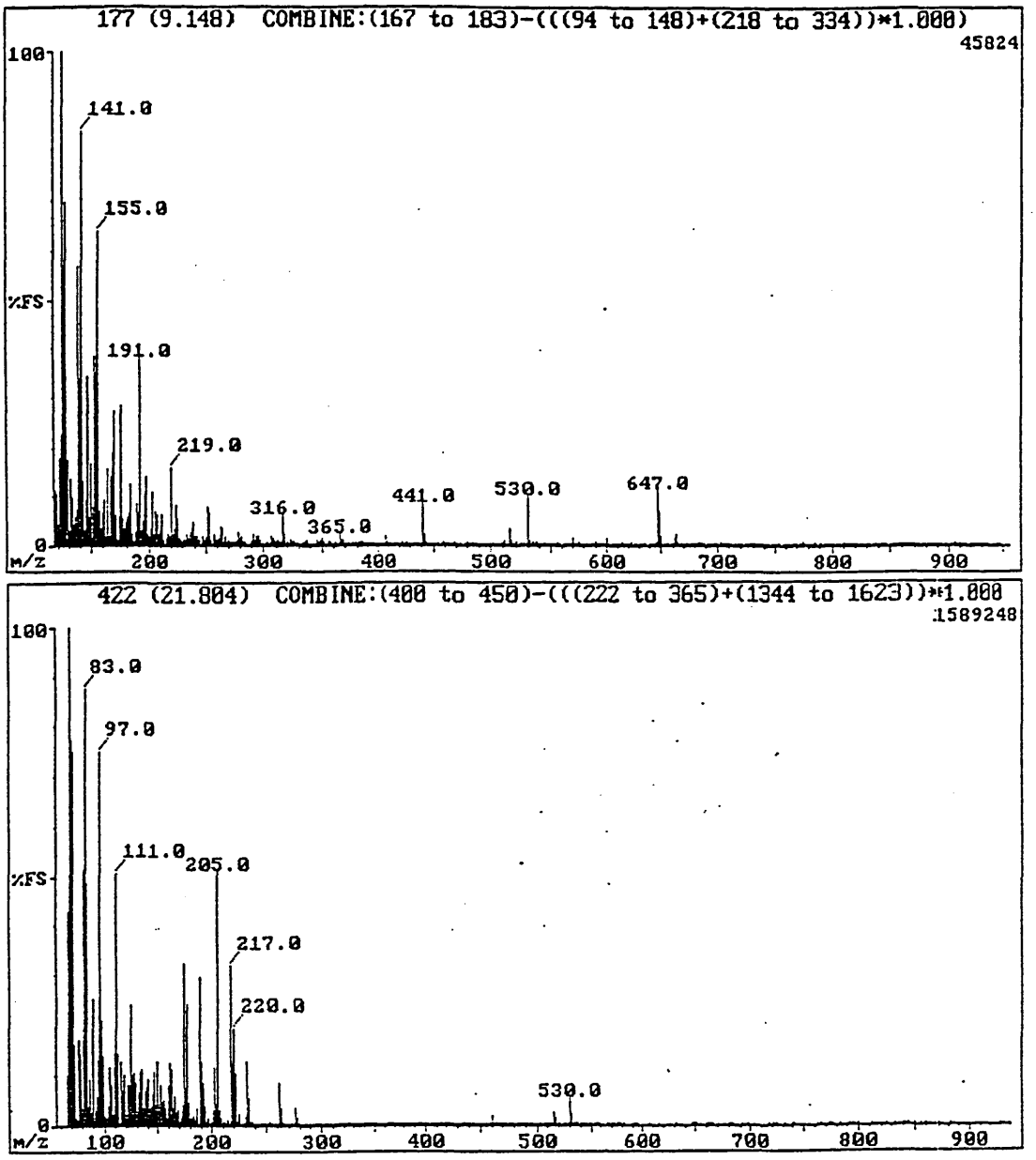


FIGURE 4.30 (A) Mass spectra of some of the products of the reaction between Irganox 1076 and t-butylperoxyl radicals.

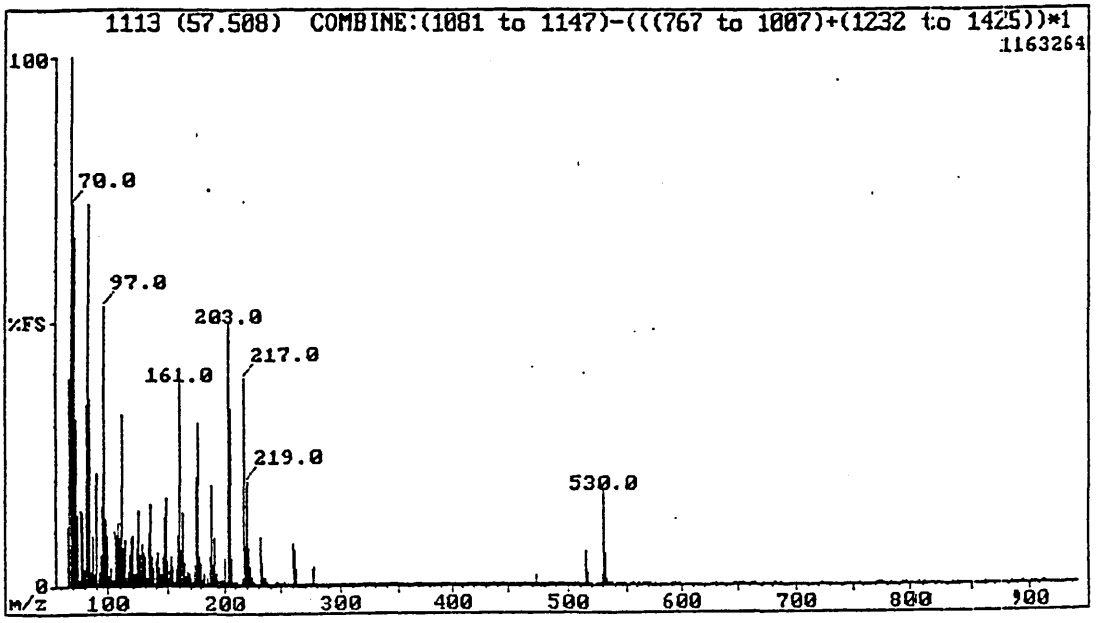

1113 (57.508) COMBINE:(1081 to 1147)-(((767 to 1007)+(1232 to 1425))*1
1163264
100
%FS
0
70.0
97.0
203.0
217.0
161.0
219.0
530.0
m/z
100
200
300
400
500
600
700
800
900

FIGURE 4.30 (B)

In addition the mixture was analysed using the modified isocratic hplc mobile phase. This revealed the presence of a further four compounds, three of which were not fully resolved from each other. This is shown in figure 4.31 which contains the isochrom display. The principal product has a UV spectrum similar to that of the conjugated bisquinonemethide (E) identified by Jonas et al.[4] In addition the product appearing at about 30 minutes has a UV spectrum similar to that of the phenol/quinone dimer identified by Jonas et al.[4] However, the identity of these compounds remains uncertain.

In conclusion, irradiation of polypropylene containing the antioxidant Irganox 1076 results in the production of a number of antioxidant-derived transformation products. In particular a product resulting from the cleavage of a t-butyl group from the parent molecule is present. This type of reaction does not appear to occur upon the thermal aging of the polymer, where the cinnamate derived from Irganox 1076 is the major product. Other minor transformation products derived from Irganox 1076 have been detected. As with Irganox 1010 the model reactions carried out do not mirror the reactions occurring in stabilized polymers.

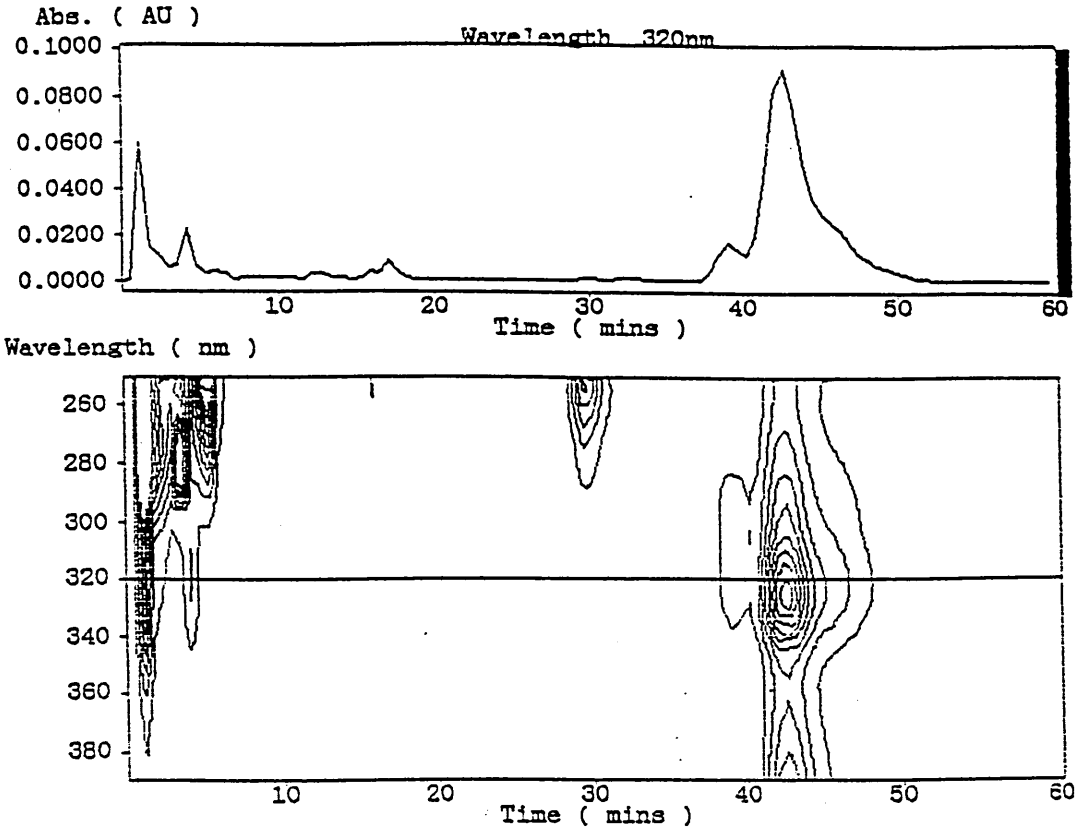


FIGURE 4.31 Isochrom display for the product mixture from the reaction between Irganox 1076 and t-butylperoxyl radicals (Isocratic hplc using the modified mobile phase).

4.4. TRANSFORMATION PRODUCTS OF IRGANOX 1330

The isocratic hplc chromatogram for the extract from polypropylene stabilized by Irganox 1330 and subjected to an irradiation dose of 50kGy is displayed in figure 4.32. At least 12 different transformation products are present in the extract and doubtless there are other products which appear together at the solvent front.

The UV spectra of some of the principal transformation products are displayed in figure 4.33 along with that of Irganox 1330 itself. A number of these spectra show two regions of intense absorption, one with an absorption maximum at about 285nm and the other with an absorption maximum at about 345nm. Absorbance in the former region probably indicates the presence of phenolic units within the transformation product similar to those contained in the structure of the parent molecule. Absorbance in the latter region probably indicates the presence of quinonoid character within the transformation products. The relative intensity of these two absorbance regions may give an indication of the number of each type of unit which is present in the molecule. A further region of absorbance with a maximum at about 255nm is also present in some of these molecules. This absorbance is probably due to $\pi \rightarrow \pi^*$ transitions occuring within the aromatic ring.

Component 1 has a UV spectrum and retention time very similar to that of 2,6-di-t-butylbenzoquinone which is known to be a transformation product of this type of antioxidant.[1]

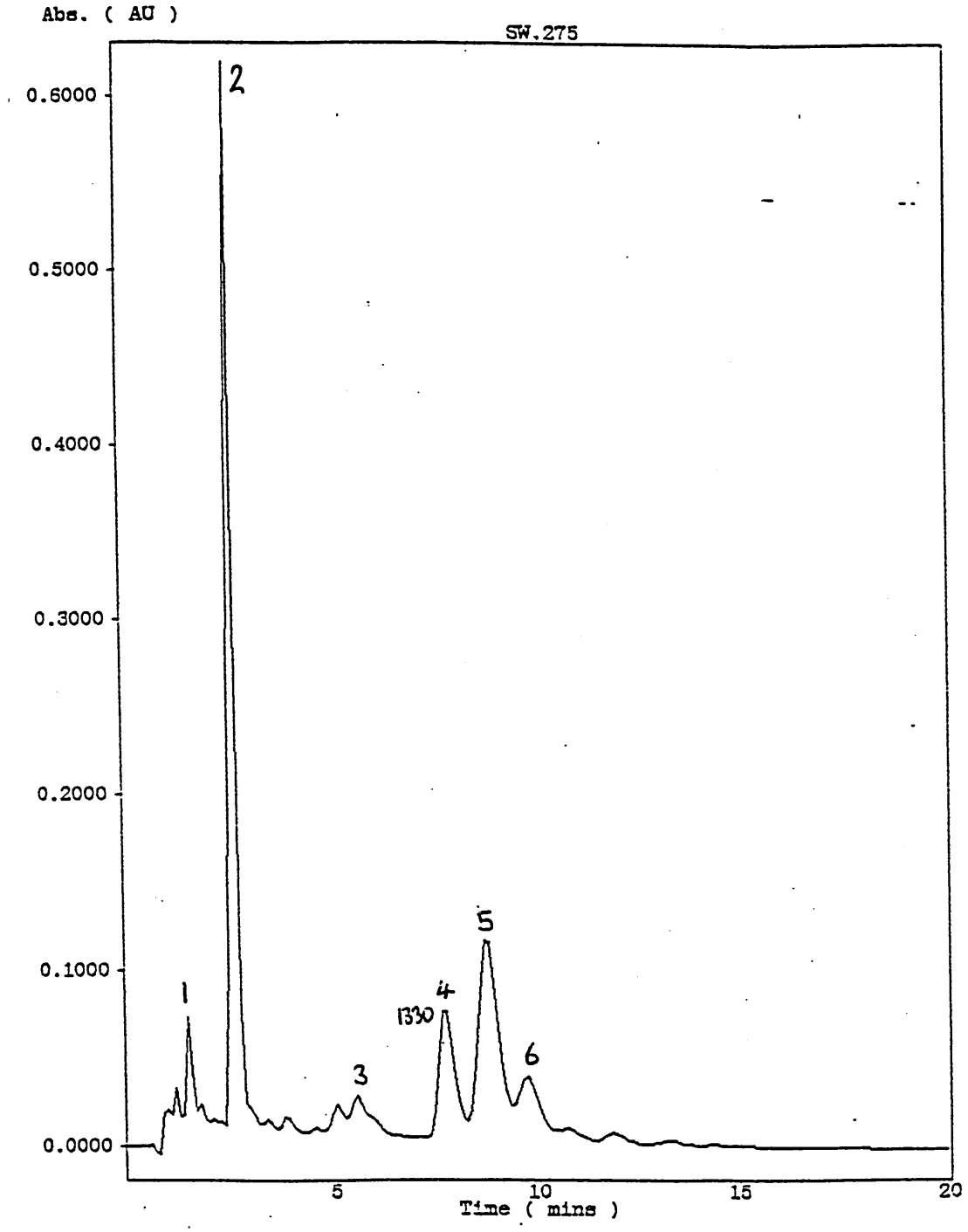


FIGURE 4.32 Isocratic hplc chromatogram of the extract from polypropylene homopolymer stabilized by Irganox 1330, subjected to an irradiation dose of 50kGy.

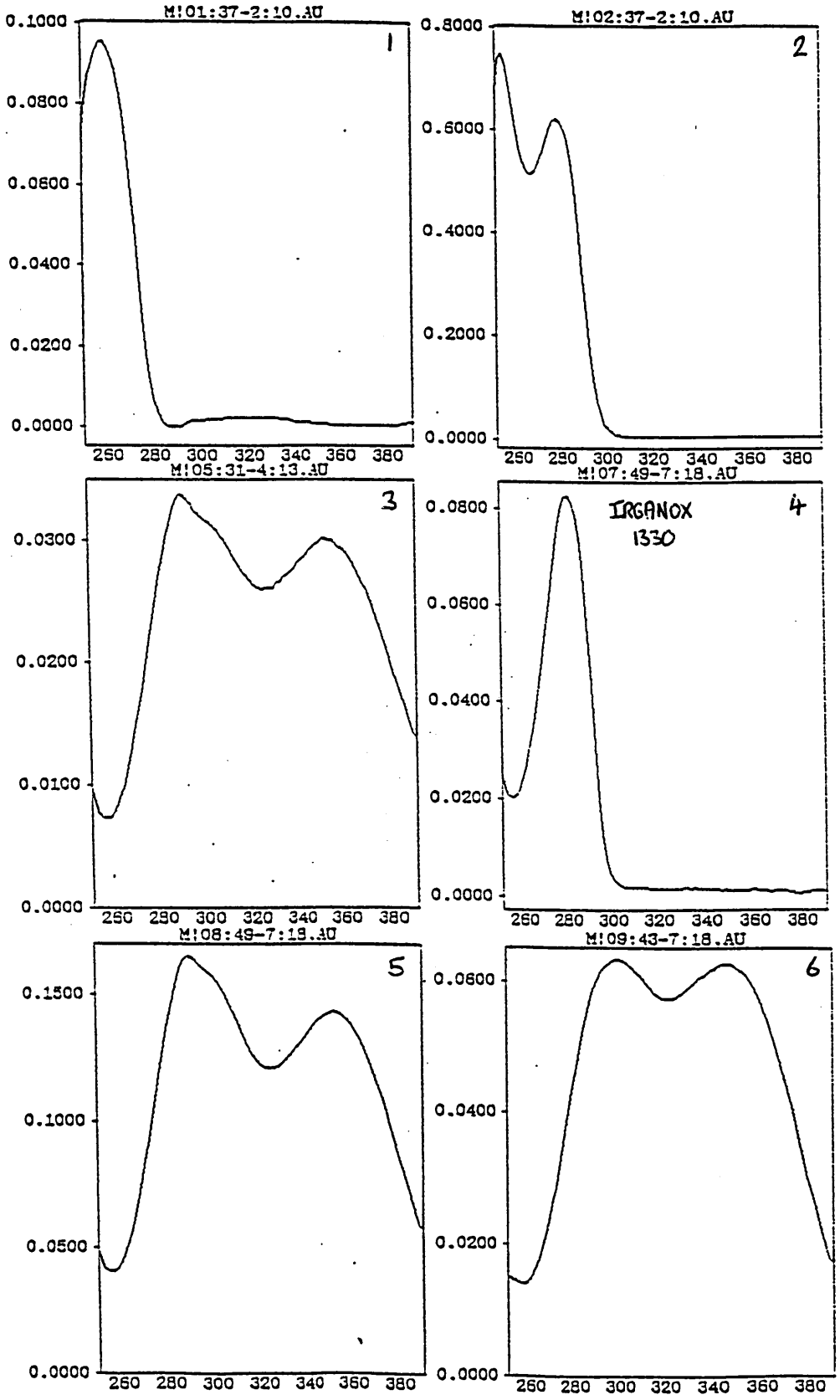


FIGURE 4.33 UV spectra of Irganox 1330 and its principal irradiation-derived transformation products

The use of gas chromatography-mass spectrometry with a 25m column revealed the presence of 1,3-di-t-butylbenzene. This seems to indicate that mechanisms other than oxidative transformation occur upon irradiation. GC using a 5m column revealed the presence of 2,6-di-t-butylbenzoquinone. This compound was also present in the unirradiated polymer but to much smaller extent. Aside from these two, no other transformation products were detected using gas chromatography. this indicates that the other transformation products known to be present are of low volatility due to either high molecular mass or high polarity.

Using the gradient hplc system, detailed in section 2.8, reveals that as with the other antioxidants, the situation is much more complex, there being many other minor transformation products formed. The chromatogram at 275nm produced using this system is presented in figure 4.34.

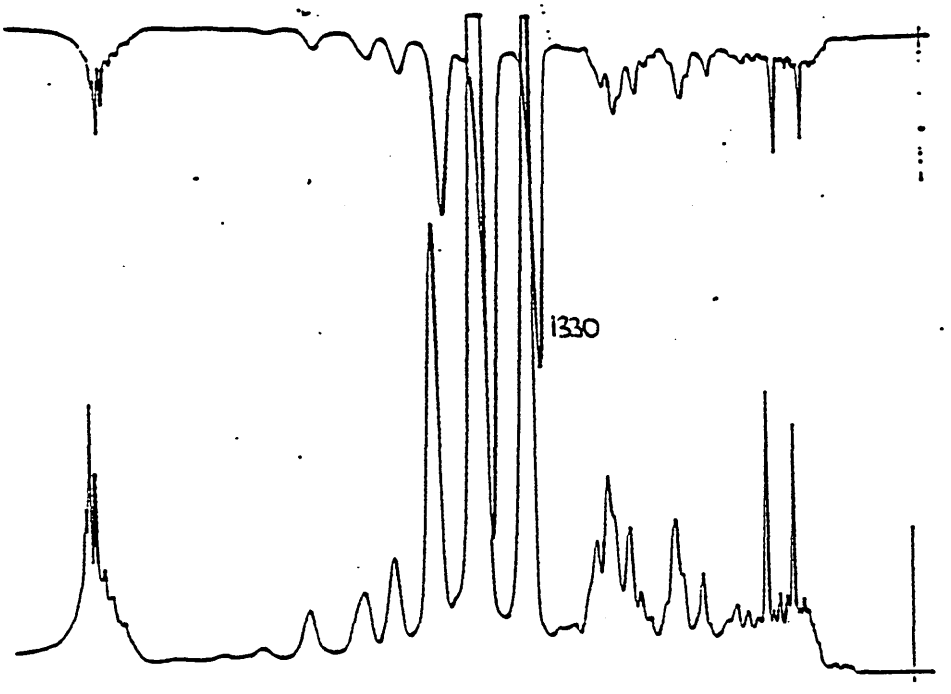


FIGURE 4.34 Gradient hplc chromatogram of the extract from polypropylene homopolymer stabilized by Irganox 1330, subjected to an irradiation dose of 50kGy.

An hplc-ms investigation of this extract was carried out according to the method detailed in section 2.9. The resulting total ion chromatogram is contained in figure 4.35. A selection of the mass spectra obtained from this chromatogram, each showing clear molecular ion peaks are presented in figure 4.36 including that for Irganox 1330. Figure 4.37 shows the structures which have been proposed for these transformation products. The structures proposed are consistent with the UV and mass spectral data, They are also consistent with the type of structures suggested by Koch for compounds arising from the oxidation of Irganox 1330 present as stabilizer in polypropylene at 200°C in air [8] (see figure 1.3).

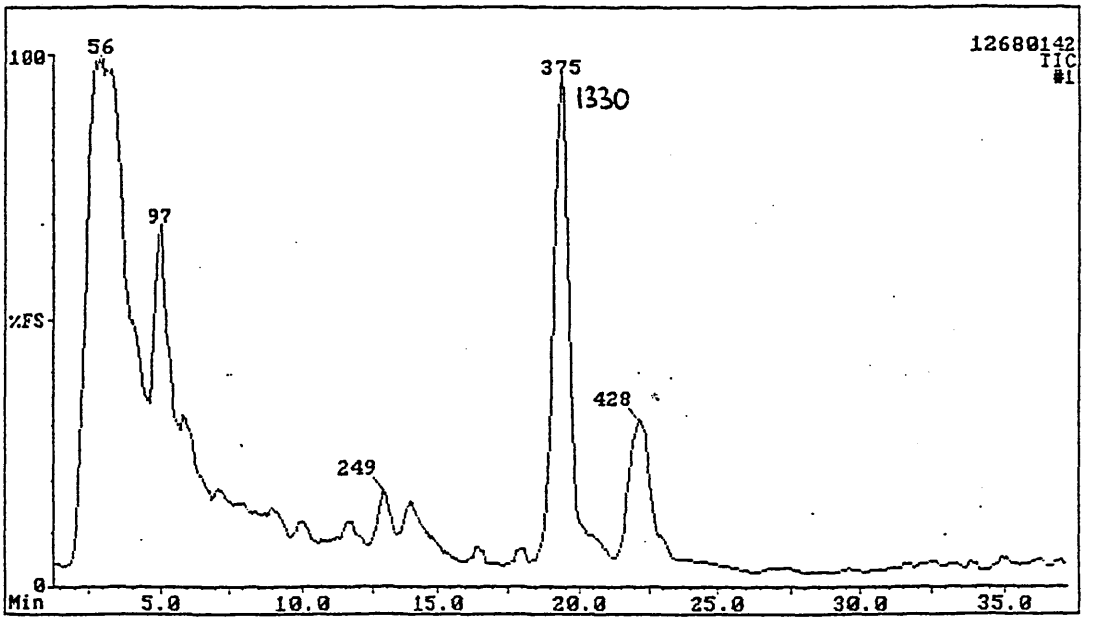


FIGURE 4.35 LC-MS TIC of the extract from polypropylene homopolymer stabilized by Irganox 1330, subjected to an irradiation dose of 50kGy.

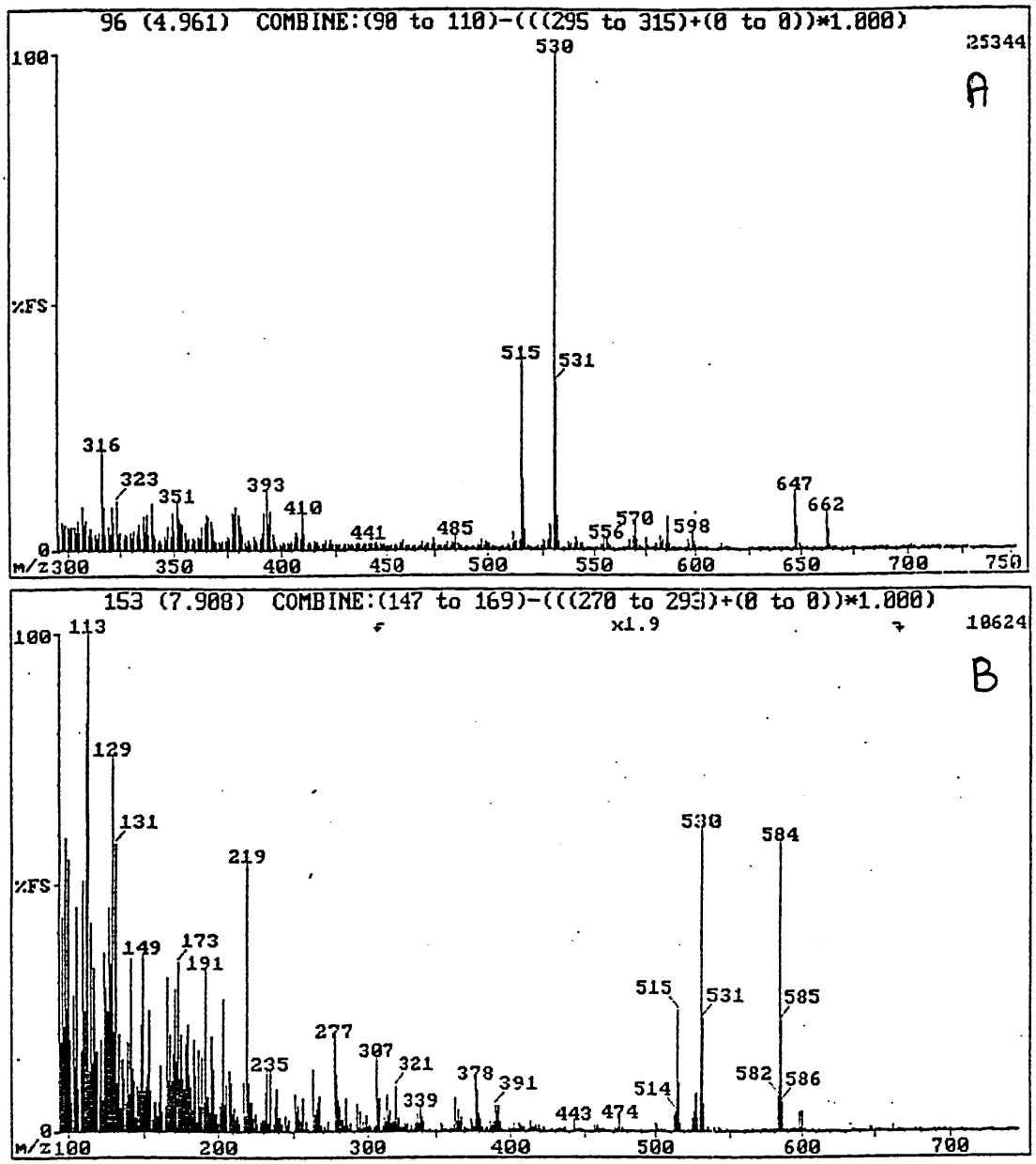


FIGURE 4.36 (A) Mass spectra obtained for some of the irradiation-derived transformation products of Irganox 1330.

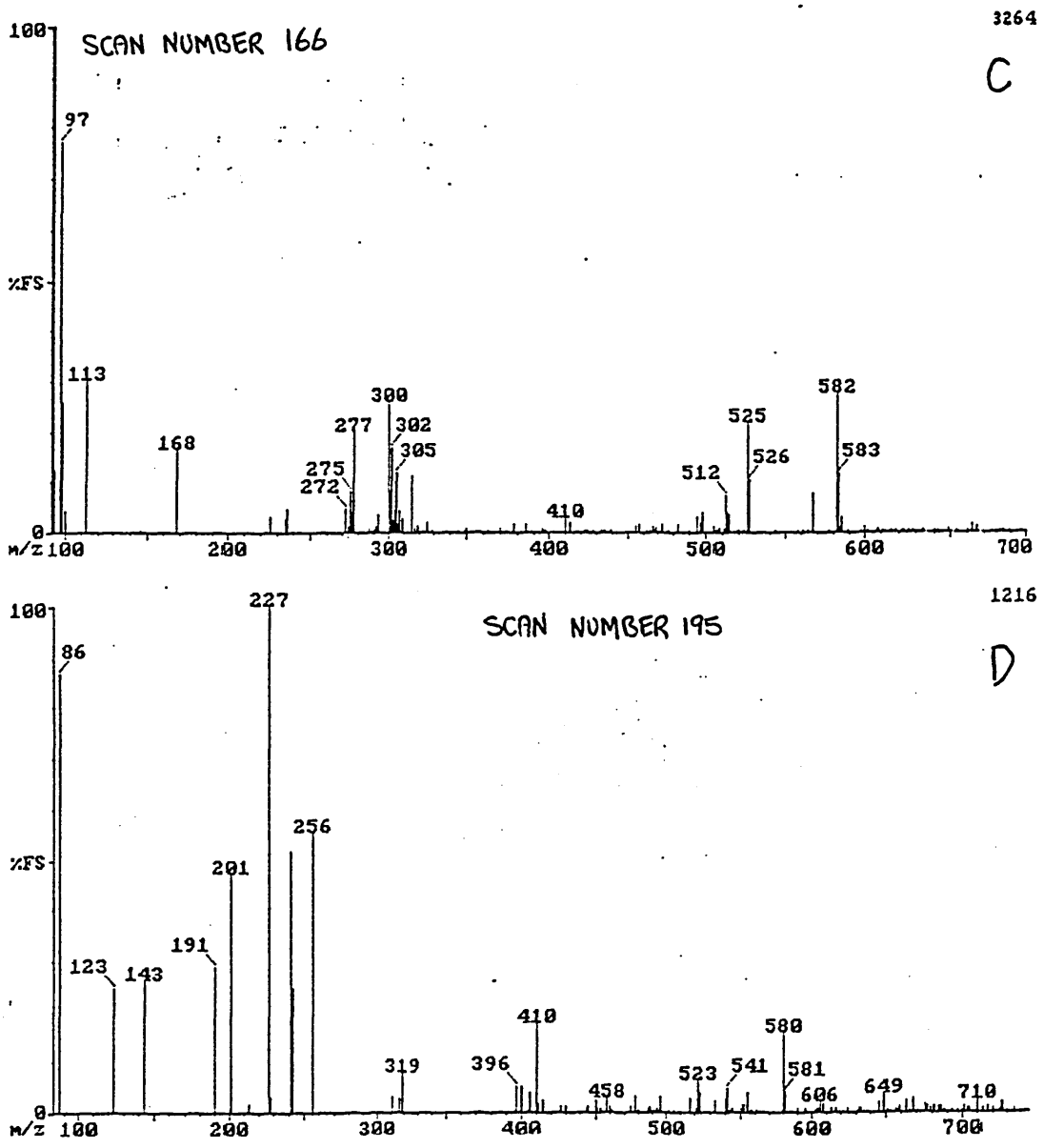

SCAN NUMBER 166
3264
C
100
%FS
0
m/z
97
113
168
275
272
277
300
302
305
410
512
525
526
582
583
100
200
300
400
500
600
700
SCAN NUMBER 195
1216
D
227
86
256
201
191
123
143
319
396
410
458
523
541
580
581
606
649
710

FIGURE 4.36 (B)

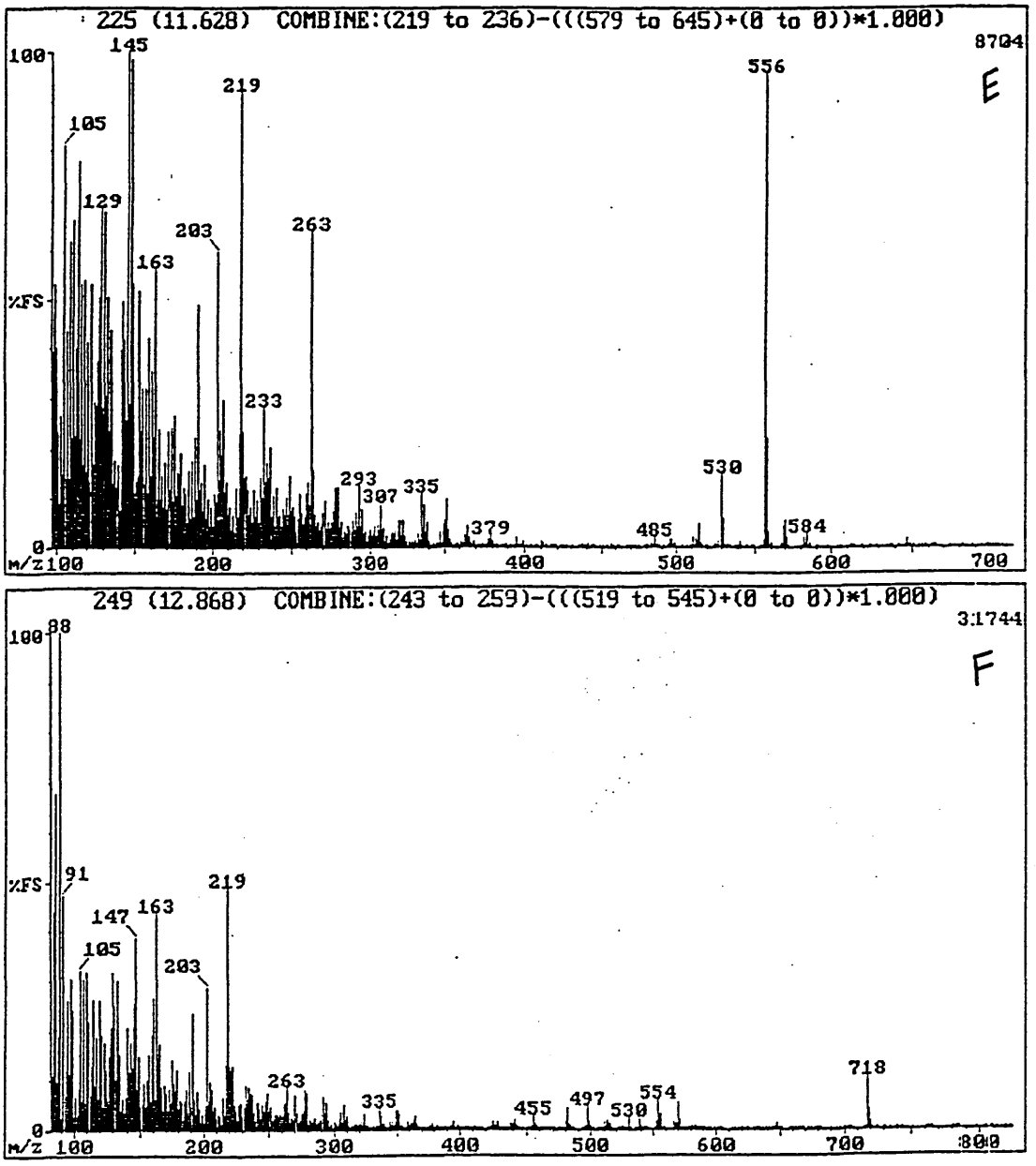

225 (11.628) COMBINE:(219 to 236)-(((579 to 645)+(0 to 0))*1.000)
8704
E
100
%FS
0
m/z
145
105
129
203
163
219
263
233
293
307
335
379
485
530
556
584
100
200
300
400
500
600
700
249 (12.868) COMBINE:(243 to 259)-(((519 to 545)+(0 to 0))*1.000)
3:1744
F
88
91
147
163
105
203
219
263
335
455
497
530
554
718
800

FIGURE 4.36 (C)

FIGURE 4.36 (D)

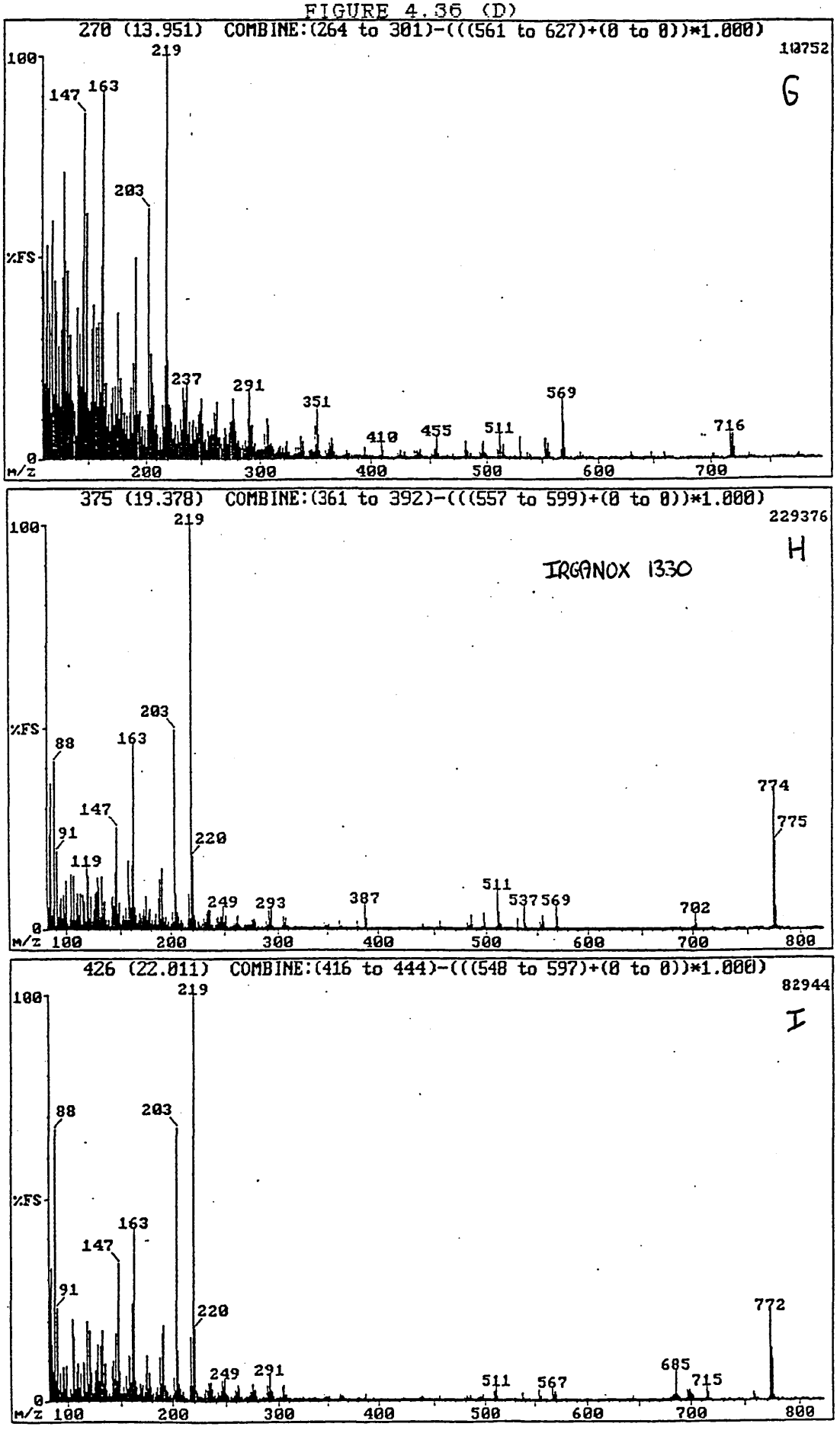
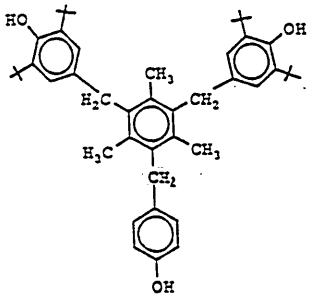
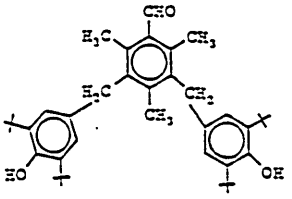

270 (13.951) COMBINE:(264 to 301)-(((561 to 627)+(0 to 0))*1.000)
10752
G
100
%FS
0
m/z
219
147
163
203
237
291
351
410
455
511
569
716
200
300
400
500
600
700
375 (19.378) COMBINE:(361 to 392)-(((557 to 599)+(0 to 0))*1.000)
229376
H
IRGANOX 1330
219
203
88
163
147
91
119
220
249
293
387
511
537
569
702
774
775
100
200
300
400
500
600
700
800
426 (22.011) COMBINE:(416 to 444)-(((548 to 597)+(0 to 0))*1.000)
82944
I
219
88
203
163
147
91
220
249
291
511
567
685
715
772

FIGURE 4.37

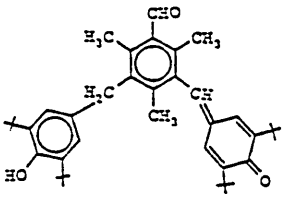
STRUCTURES PROPOSED FOR THE IRRADIATION-DERIVED TRANSFORMATION PRODUCTS OF IRGANOX 1330



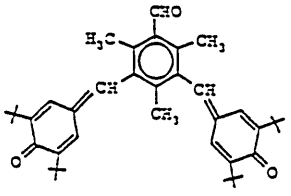
A RMM = 662



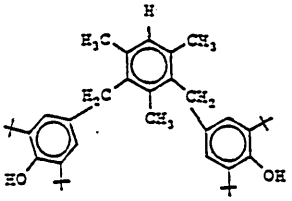
B RMM = 584



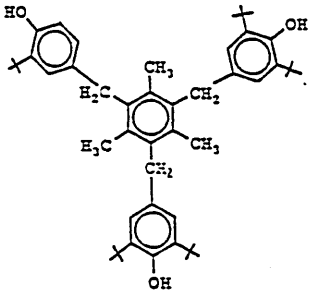
C RMM = 582



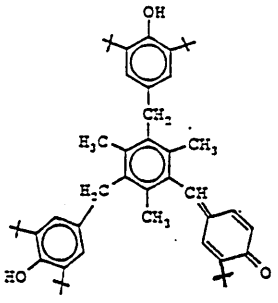
D RMM = 580



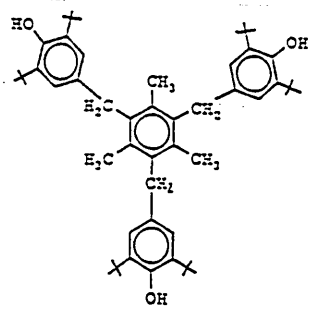
E RMM = 556



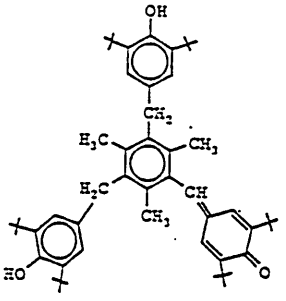
F RMM = 718



G RMM = 716



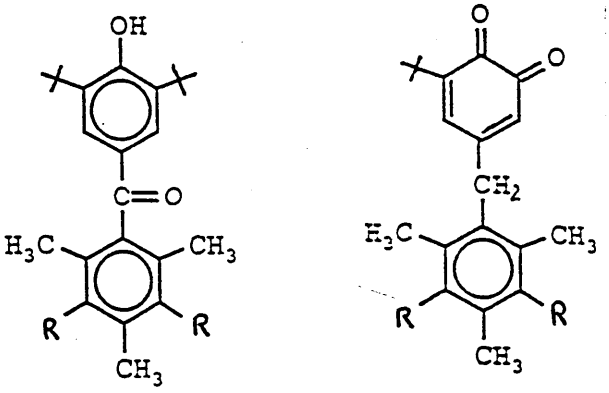
H RMM = 774



I RMM = 772

1330

Koch also suggests that structures of the following types are produced:



However, these compounds have not been detected during the present study of extracts of irradiated polymers. It is of interest that Koch did not report the formation of products where tertiary butyl groups have been removed and replaced by hydrogen atoms, such as those with relative molecular masses of 662, 716 and 718. This kind of reaction appears to be characteristic of the irradiation-induced transformation of antioxidants of this type present in polyolefins.

For comparison, a sample of polypropylene stabilized by Irganox 1330 was subjected to the thermal aging process detailed in section 2.12.

The resulting isocratic hplc chromatogram, produced using the method detailed in section 2.8, is displayed in figure 4.38. The chromatograms from extracts arising from the same polymer before either irradiation or thermal treatment, and after an irradiation dose of 50kGy, are also displayed in figure 4.38 for comparison. The retention times for the Irganox 1330 peaks do not coincide exactly since the samples were not chromatographed consecutively.

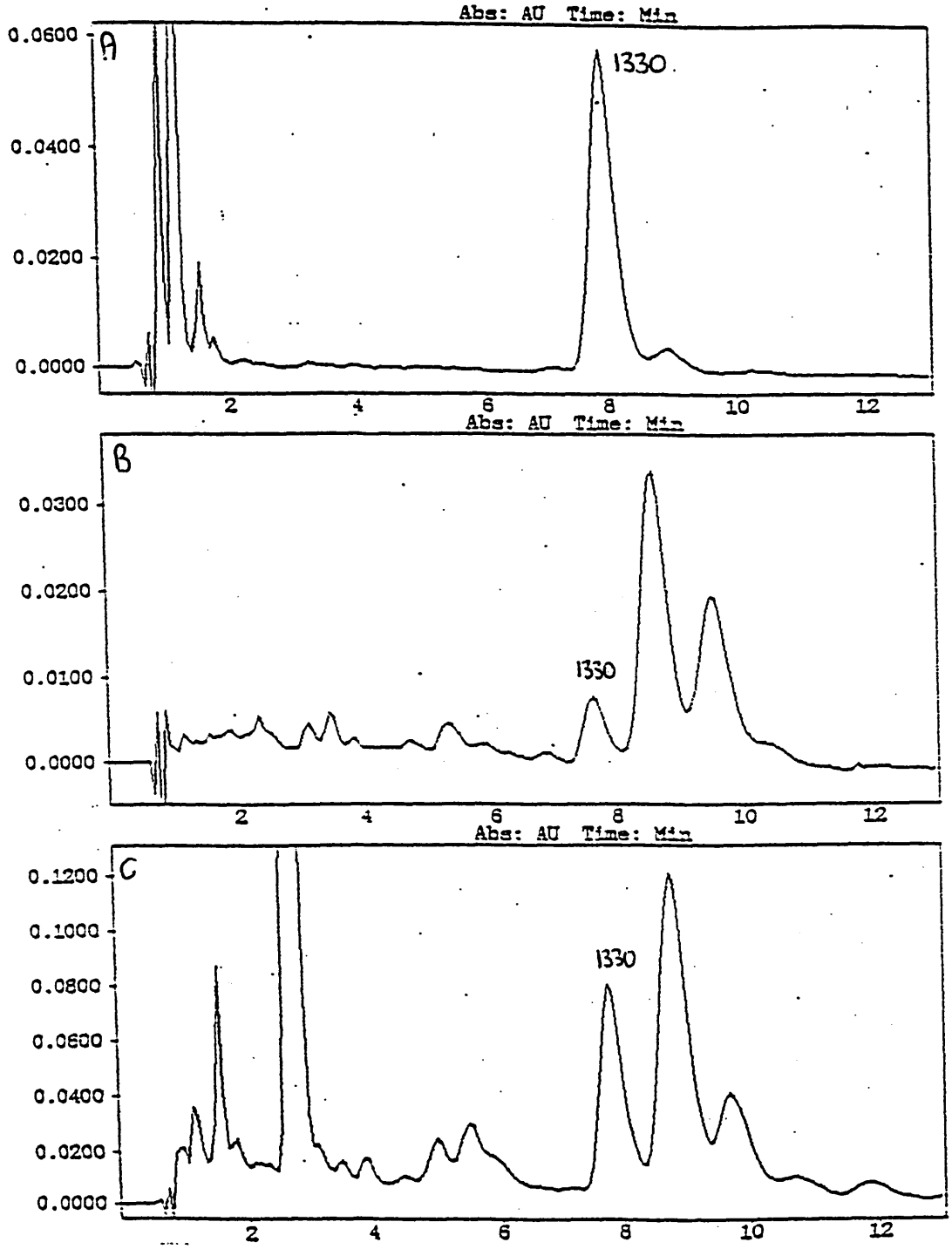


FIGURE 4.38 A) Hplc chromatogram of the extract from 0kGy PP(H) containing 1330
-no thermal treatment
B) Hplc chromatogram of the extract from 0kGy PP(H) containing 1330
- after 125 hours at 150°C in air
C) Hplc chromatogram of the extract from 50kGy PP(H) containing 1330
- no thermal treatment

The untreated sample contains traces of three minor compounds and a larger peak near the solvent front which is probably due to 2,6-di-t-butylbenzoquinone. These compounds are almost certainly present as a consequence of the initial thermal processing. Judging from the chromatograms and UV spectra thermal treatment and irradiation produce a very similar range of transformation products, with the exception that irradiation results in the production of a range of compounds which have lost one or more tertiary butyl groups. This was confirmed by LC-MS investigations.

A model study involving the reaction of Irganox 1330 with tert-butylperoxyl radicals was also carried out, using the method detailed in section 2.13. The chromatogram of the resulting reaction mixture, analysed using the isocratic hplc technique detailed in section 2.8, is shown in figure 4.39. Peak 1 is probably impure.

This process results in the production of at least twelve different compounds. The UV spectra of five of the principal products are given in figure 4.40.

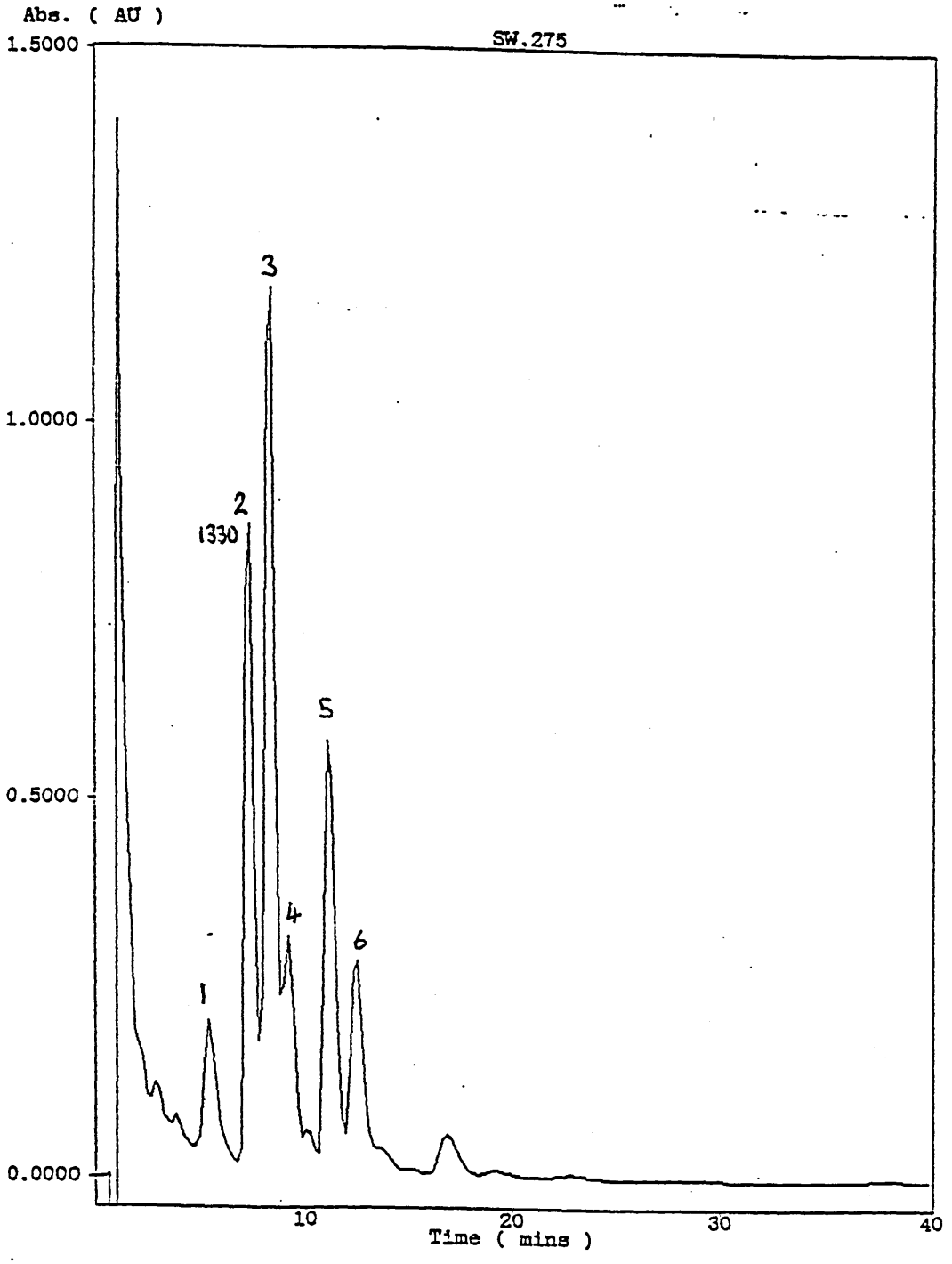


FIGURE 4.39 Isocratic hplc chromatogram obtained for the product mixture of the reaction between Irganox 1330 and t-butylperoxyl radicals.

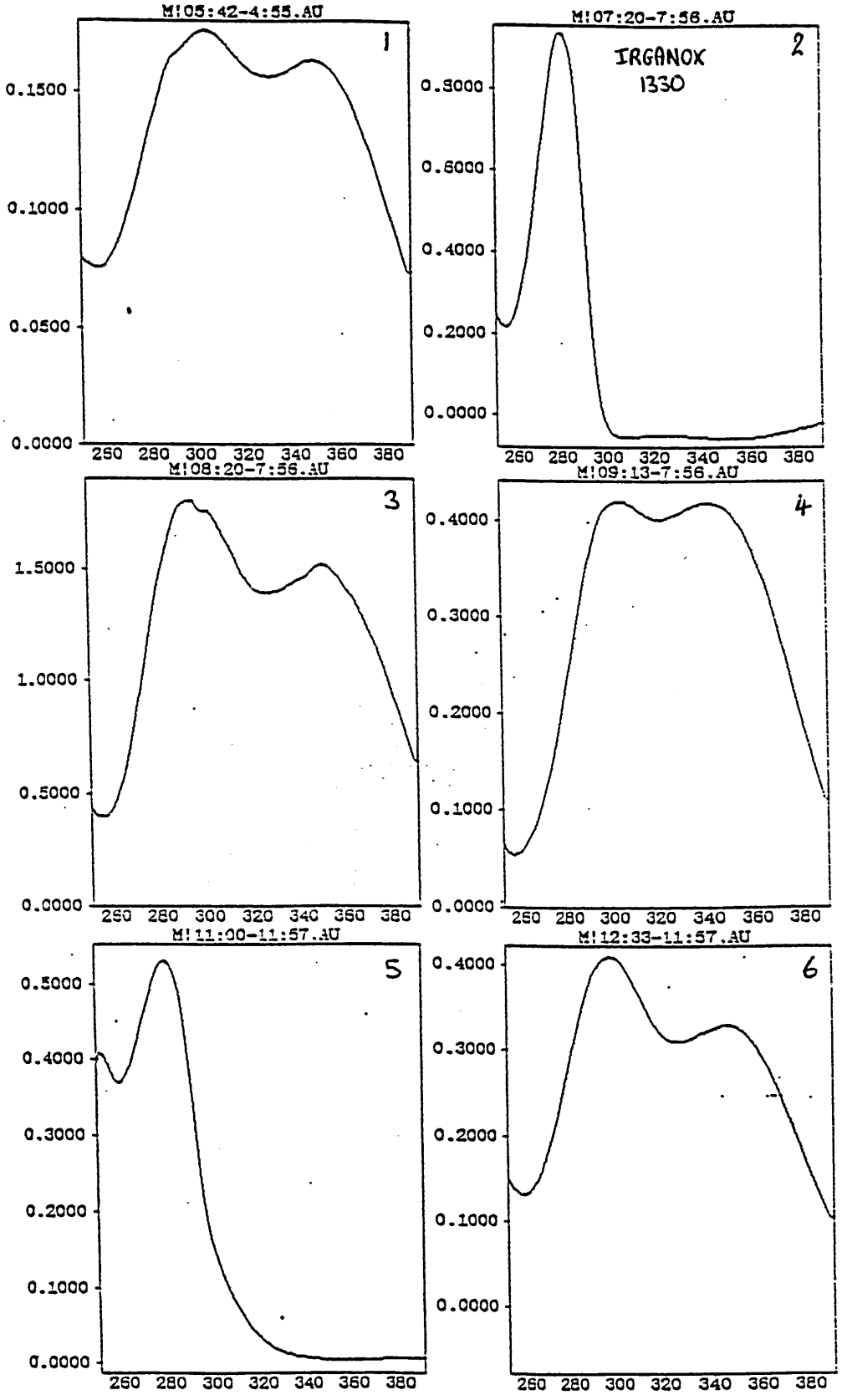


FIGURE 4.40 UV spectra of the principal products of the reaction between Irganox 1330 and t-butylperoxyl radicals.

The retention times and UV data suggest that some of these compounds are similar to those produced by the irradiation and thermal treatments of Irganox 1330 present in polypropylene, whilst others are different. The LC-MS data resulting from this sample confirms this. The TIC is displayed in figure 4.41 and figure 4.42 shows a selection of mass spectra obtained. The products with scan numbers of 598 and 675 probably have molecular masses above 1000 units.

The reaction of Irganox 1330 with t-butylperoxyl radicals does not, however, result in the formation of products which have lost t-butyl groups, such as those formed on irradiation.

In conclusion, irradiation of polypropylene containing the antioxidant Irganox 1330 results in the production of a number of antioxidant-derived transformation products. Structures have been suggested for some of these products including some which arise from the cleavage of t-butyl groups. Compounds of this type do not appear to be produced upon thermal aging of the same polymer. Many of the products appear to contain quinonoid functionalities. The model reaction between Irganox 1330 and t-butylperoxyl radicals appears to produce a range of compounds, some of which are similar to those produced in the stabilized polymers. However, compounds resulting from the cleavage of t-butyl groups are not formed under these conditions.

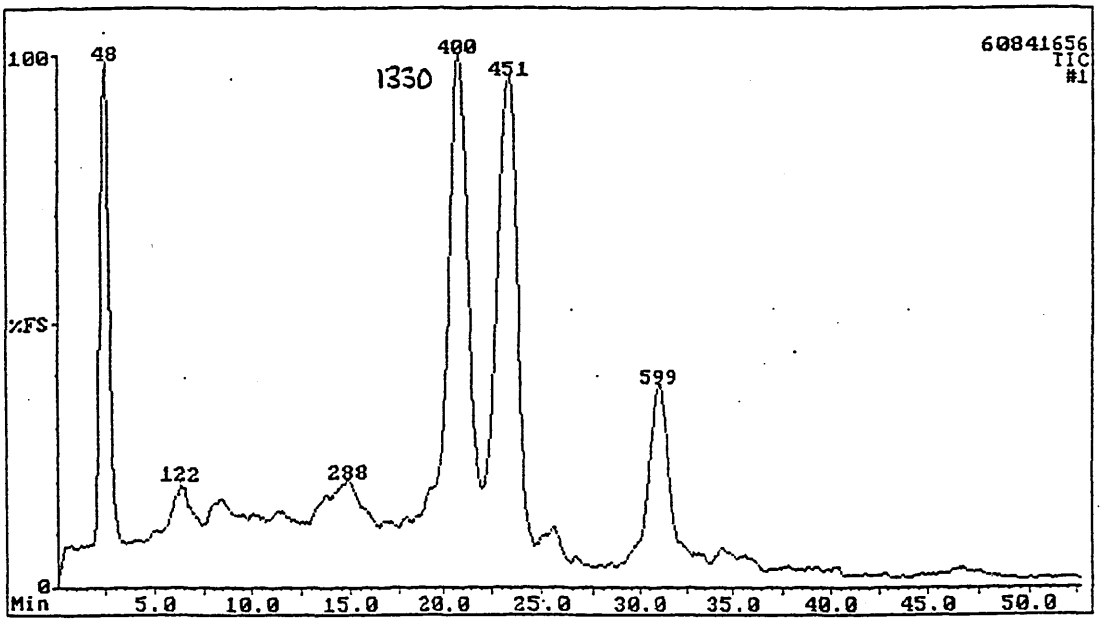


FIGURE 4.41 LC-MS TIC for the product mixture of the reaction between Irganox 1330 and t-butylperoxyl radicals.

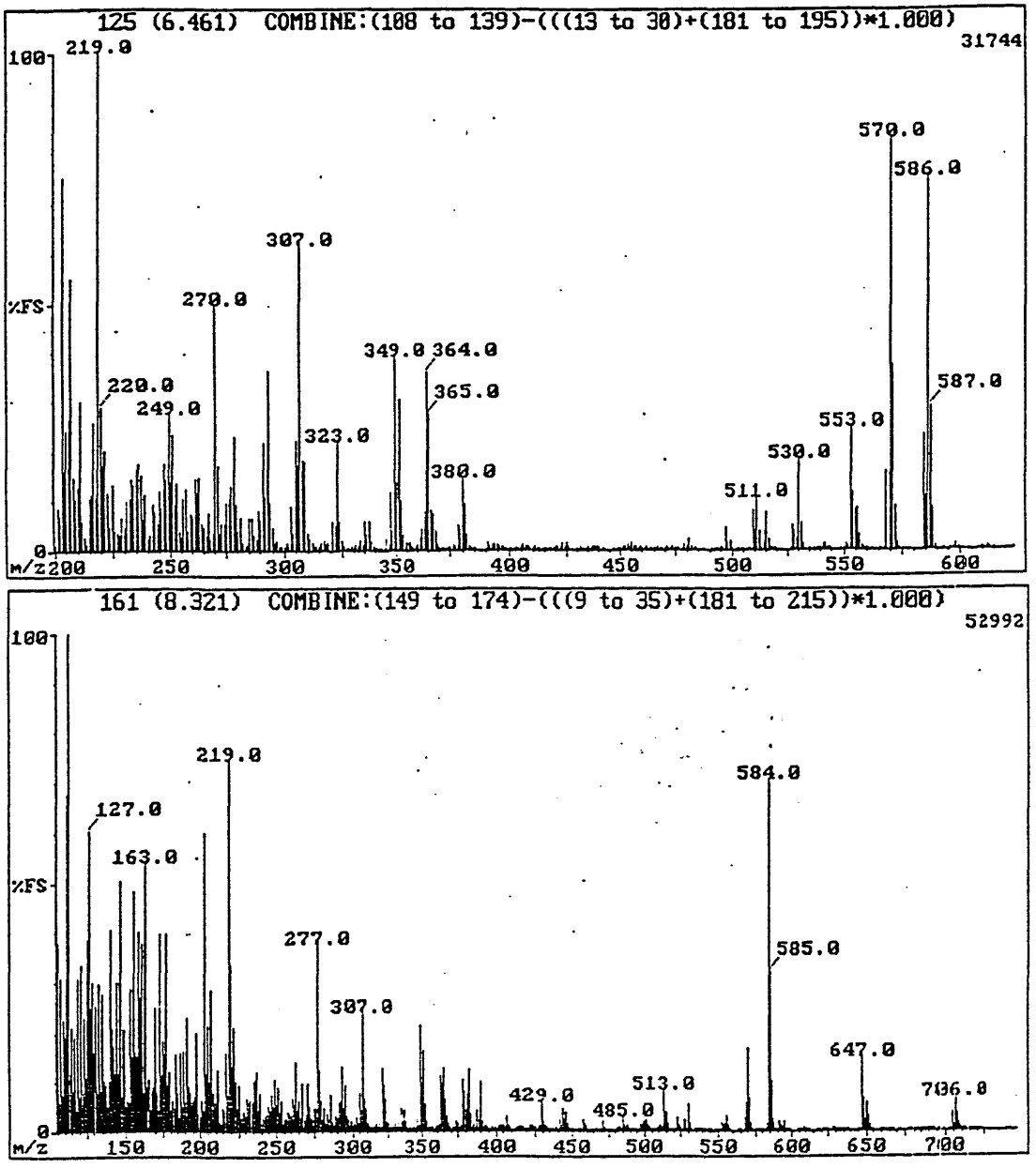


FIGURE 4.42 (A) Mass spectra of Irganox 1330 and some of the products of the reaction between Irganox 1330 and t-butylperoxyl radicals.

FIGURE 4.42 (B)

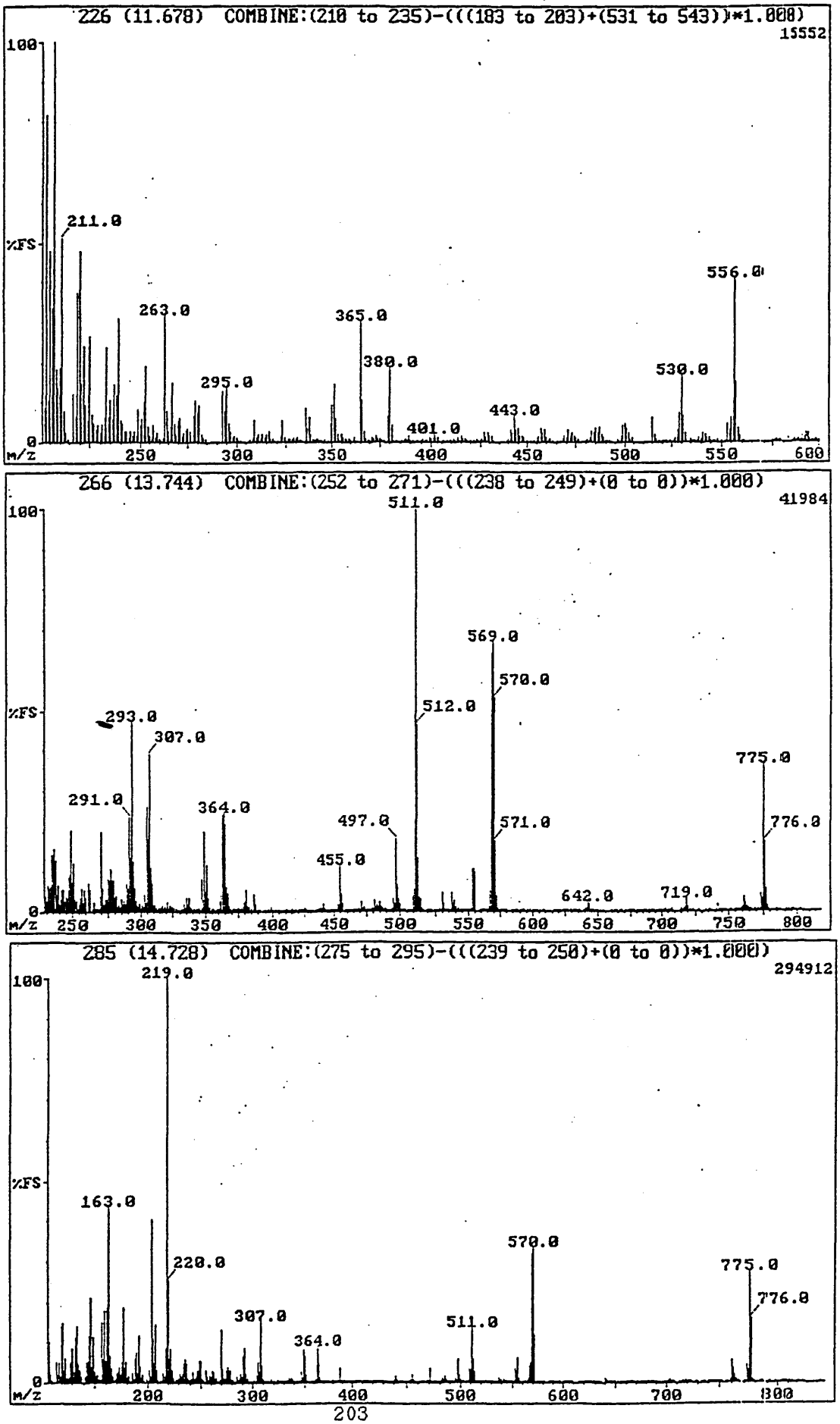
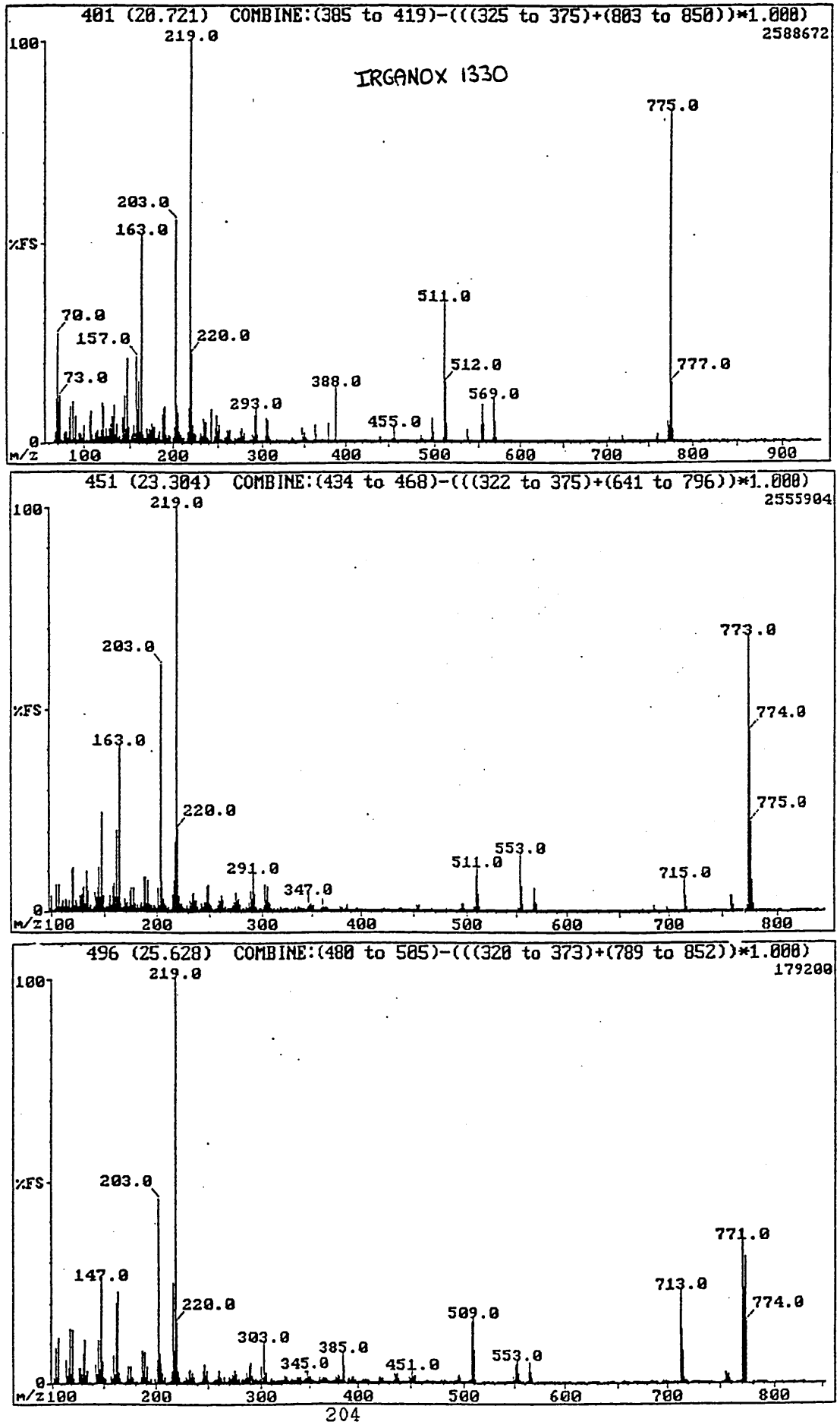

226 (11.678) COMBINE:(210 to 235)-(((183 to 203)+(531 to 543))*1.000)
15552
100
%FS
0
m/z
211.0
263.0
295.0
365.0
380.0
401.0
443.0
530.0
556.0
250
300
350
400
450
500
550
600
266 (13.744) COMBINE:(252 to 271)-(((238 to 249)+(0 to 0))*1.000)
41984
511.0
569.0
570.0
512.0
293.0
307.0
291.0
364.0
497.0
455.0
571.0
775.0
776.0
642.0
719.0
650
700
750
800
285 (14.728) COMBINE:(275 to 295)-(((239 to 250)+(0 to 0))*1.000)
294912
219.0
163.0
220.0
307.0
364.0
511.0
570.0
775.0
776.0
200

FIGURE 4.42 (C)

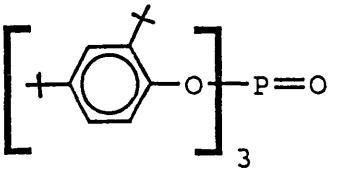

401 (20.721) COMBINE:(385 to 419)-(((325 to 375)+(803 to 850))*1.000)
2588672
IRGANOX 1330
219.0
775.0
203.0
163.0
511.0
70.0
157.0
220.0
512.0
777.0
73.0
388.0
569.0
293.0
455.0
%FS
m/z
451 (23.304) COMBINE:(434 to 468)-(((322 to 375)+(641 to 796))*1.000)
2555904
219.0
773.0
203.0
774.0
163.0
775.0
220.0
553.0
511.0
291.0
715.0
347.0
%FS
m/z
496 (25.628) COMBINE:(480 to 585)-(((320 to 373)+(789 to 852))*1.000)
179200
219.0
203.0
771.0
147.0
713.0
774.0
220.0
509.0
303.0
385.0
345.0
451.0
553.0
%FS
m/z

4.5 TRANSFORMATION PRODUCTS OF IRGAFOS 168

The isocratic hplc chromatogram of the extract from polypropylene stabilized by Irgafos 168 and subjected to an irradiation dose of 50kGy is displayed in figure 4.43. At least 18 different transformation products are present in the extract, and once again, there are certainly other products which appear together at the solvent front.

UV spectra of the principal products which are fully separated from the solvent front are displayed in figure 4.44, together with that of Irgafos 168.

The UV spectra contain three basic types of absorbance. The absorption peak which occurs at about 275nm is due to the presence of the aromatic ring linked to the bridging oxygen. The absorption peak which occurs at about 255nm is due to $\pi \rightarrow \pi^*$ transitions within the aromatic ring. Any absorption which occurs above about 300nm is probably due to the presence of some quinonoid units. Component 5 has a UV spectrum identical to that of the phosphate derived from Irgafos 168.[9] The structure of the phosphate is given below :-



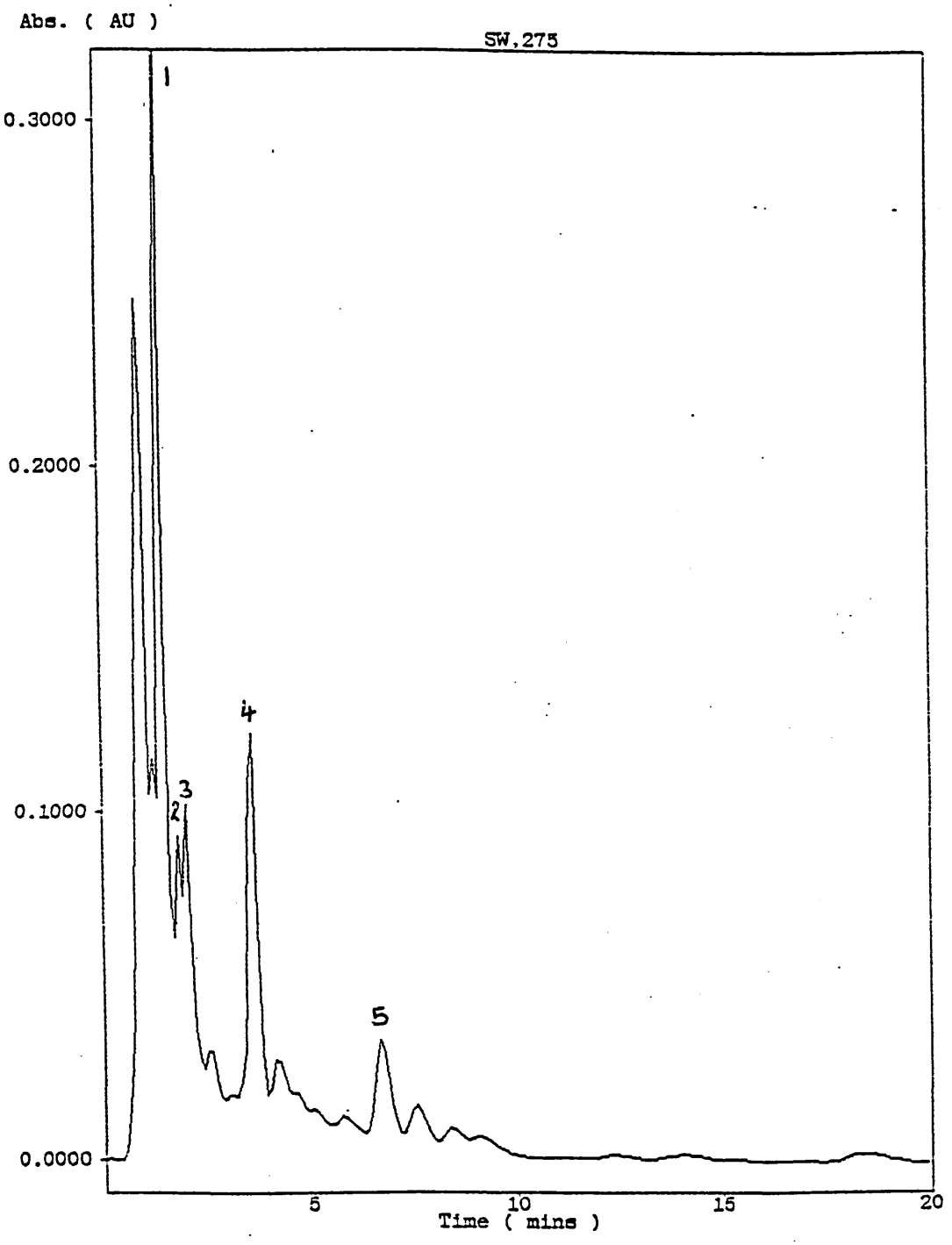


FIGURE 4.43 Isocratic hplc chromatogram of the extract from polypropylene homopolymer stabilized by Irgafos 168, subjected to an irradiation dose of 50kGy.

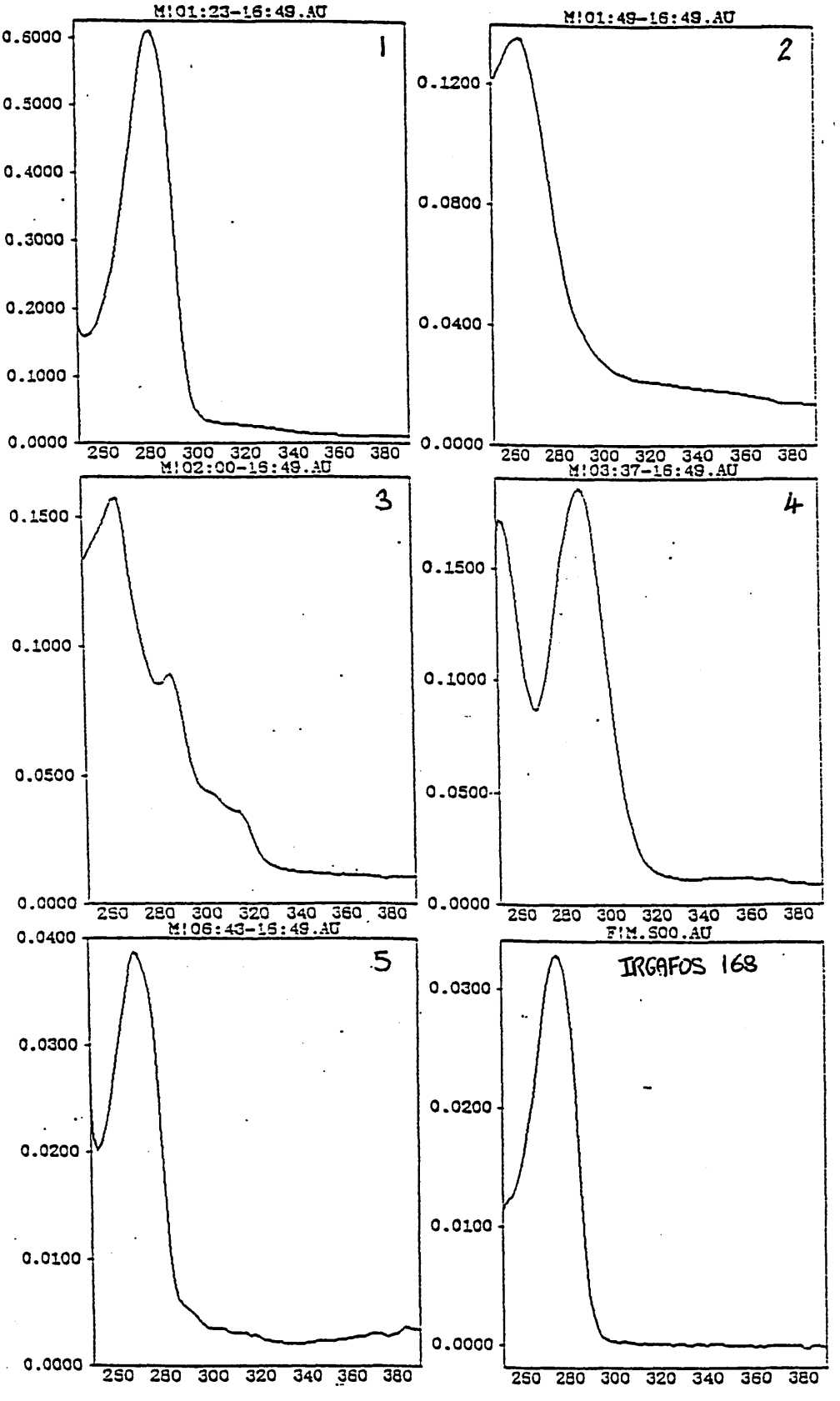


FIGURE 4.44 UV spectra of Irgafos 168 and its principal irradiation-derived transformation products.

Component 1 has a UV spectrum very similar to that of BHT and a very similar retention time. It is therefore likely that this product is 2,4-di-t-butylphenol.

Gas chromatography - mass spectrometry using the 25m long column (see section 2.7) revealed the presence of 2,4-di-t-butylphenol in this extract, confirming the deductions made from the UV spectra and the retention time of component 1 in the isocratic hplc chromatogram. The use of a 5m long column enabled the detection of two compounds, other than Irgafos 168, in an extract from a sample of unirradiated polypropylene stabilized by Irgafos 168. These compounds were the phosphate derived from Irgafos 168 and a product with a molecular ion at 342 mass units, which remains unidentified.

Extracts from polypropylene samples stabilized by Irgafos 168 and subjected to the usual range of doses of electron-beam irradiation were also analysed using ^{31}P nmr spectroscopy (see section 2.14). The ^{31}P nmr spectra were obtained under the same conditions and are displayed in figure 4.45.

The ^{31}P nmr analyses were carried out externally and unfortunately took ten months to complete. Thus these results cannot be relied upon to give quantitative data, but they do show general trends.

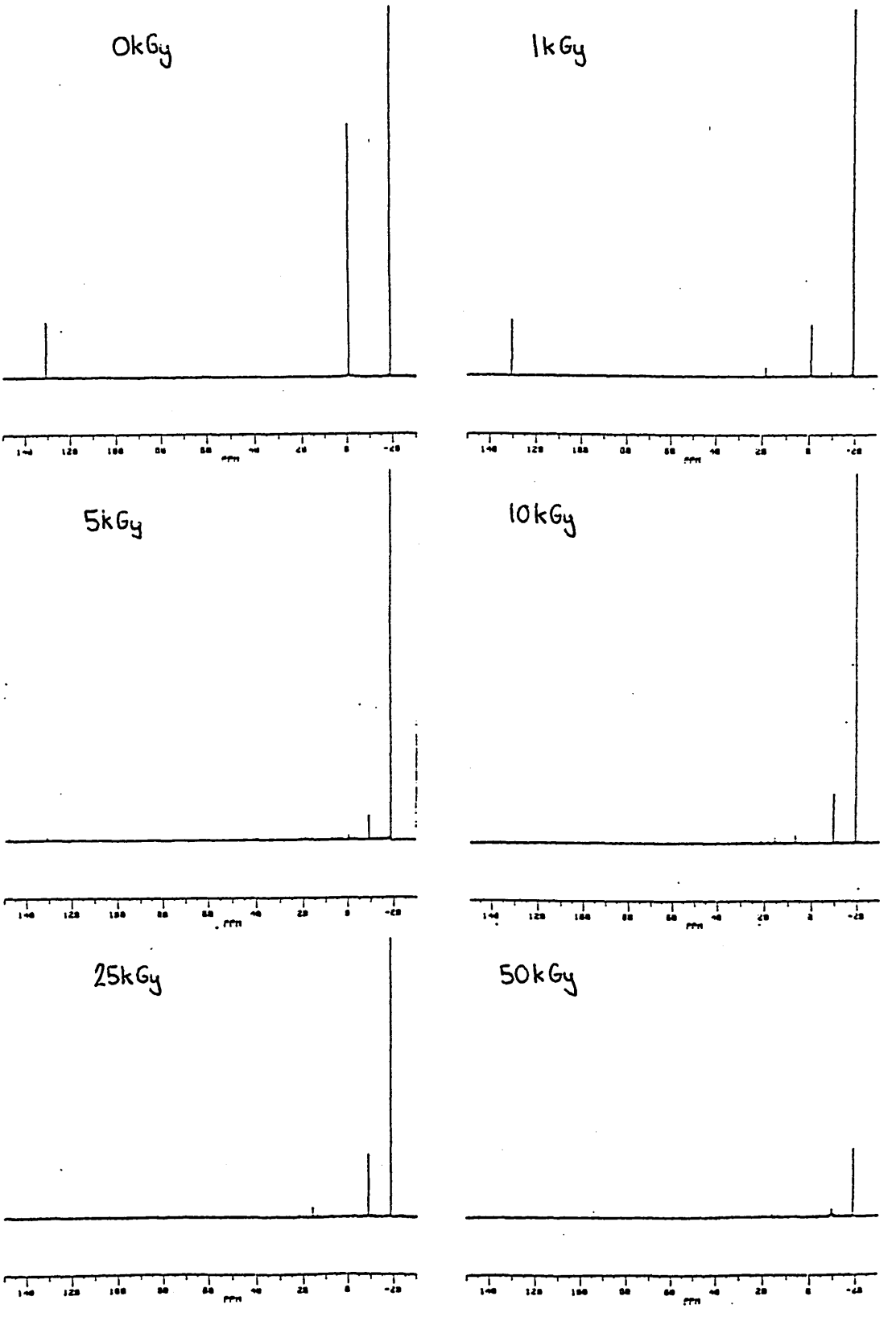


FIGURE 4.45 ^{31}P nmr spectra of extracts from polypropylene homopolymer containing Irgafos 168, subjected to a range of doses of electron-beam irradiation.

The signal due to Irgafos 168 is present at δ=131ppm and that due to the related phosphate is present at δ=-18ppm. These spectra show that Irgafos 168 is completely transformed by a dose of 10kGy and the concentration of the phosphate is markedly reduced on exposure to 50kGy of irradiation. The spectra also show the presence of at least five other phosphorus-containing transformation products which are produced on irradiation of the polymer. All the species present are markedly affected by an irradiation dose of 50kGy. The extract from the sample subjected to an irradiation 50kGy was also analysed using the gradient hplc system detailed in section 2.8. This reveals that the situation is much more complex and there are many other minor transformation products formed. The chromatogram at 275nm produced using this system is presented in figure 4.46.

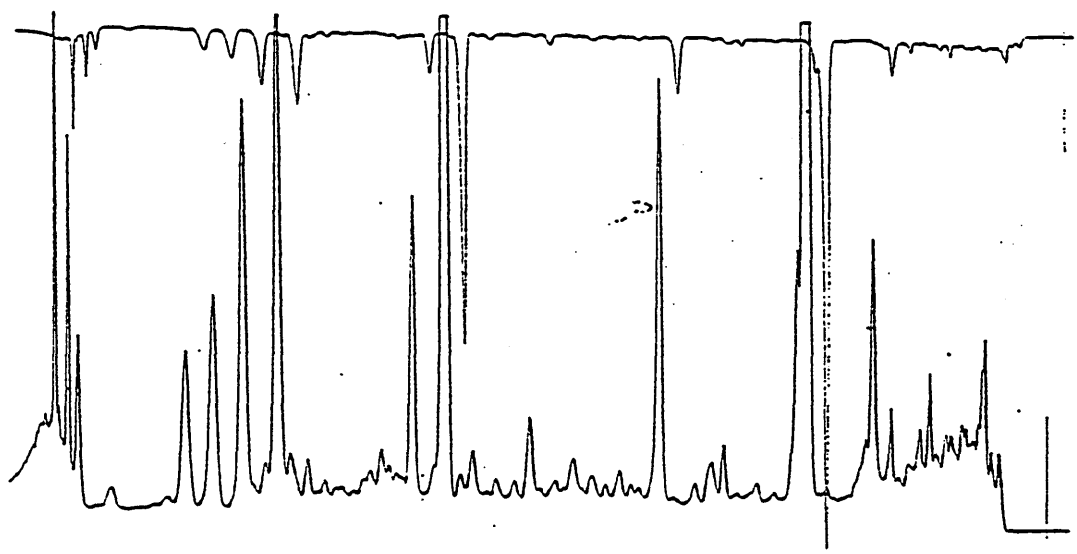


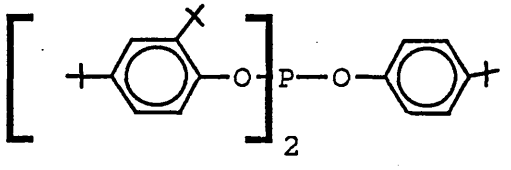
FIGURE 4.46 Gradient hplc chromatogram of the extract from polypropylene homopolymer stabilized by Irganox 168, subjected to an irradiation dose of 50kGy.

An hplc-ms investigation of this extract was carried out according to the method detailed in section 2.9. The resulting total ion chromatogram is displayed in figure 4.47.

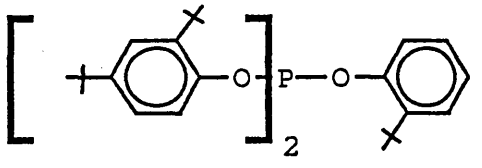
A selection of the mass-spectra obtained, showing clear molecular ions, are presented in 4.48

The product at scan number 352 has a mass spectrum identical to that of the phosphate of Irgafos 168. Two possible structures have been suggested for the product of scan number 255 which has a molecular mass of 591, i.e. (F) and (G)

(F)



(G)



These structures are a result of the loss of a tertiary butyl group from the parent molecule. As has been noted earlier, this type of process appears to be a characteristic result of irradiation.

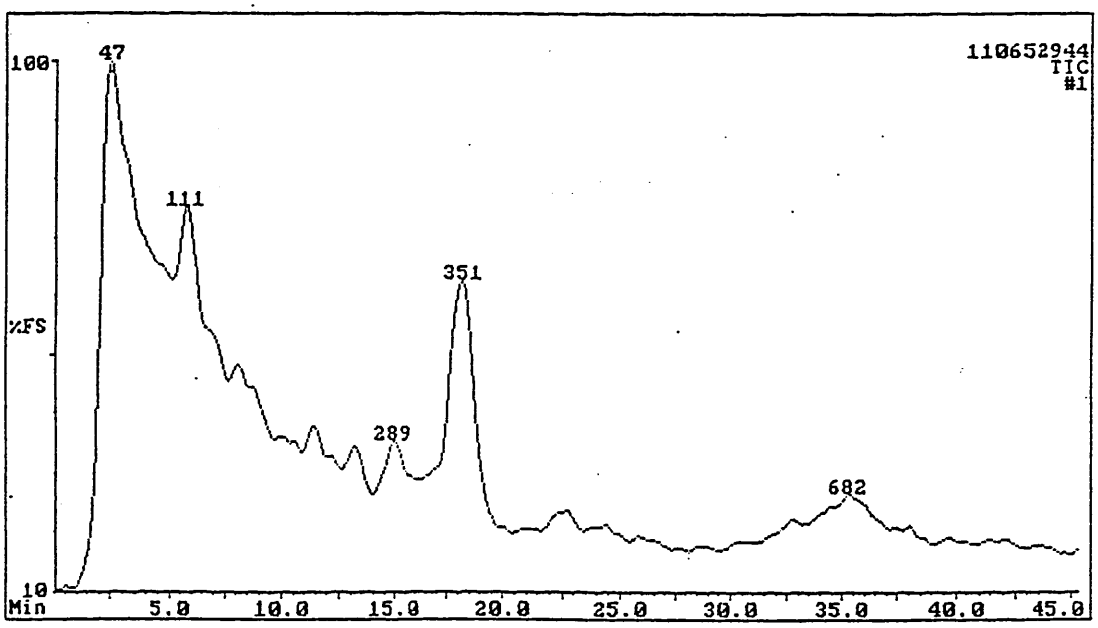


FIGURE 4.47 LC-MS TIC of the extract from polypropylene homopolymer stabilized by Irgafos 168, subjected to an irradiation dose of 50kGy.

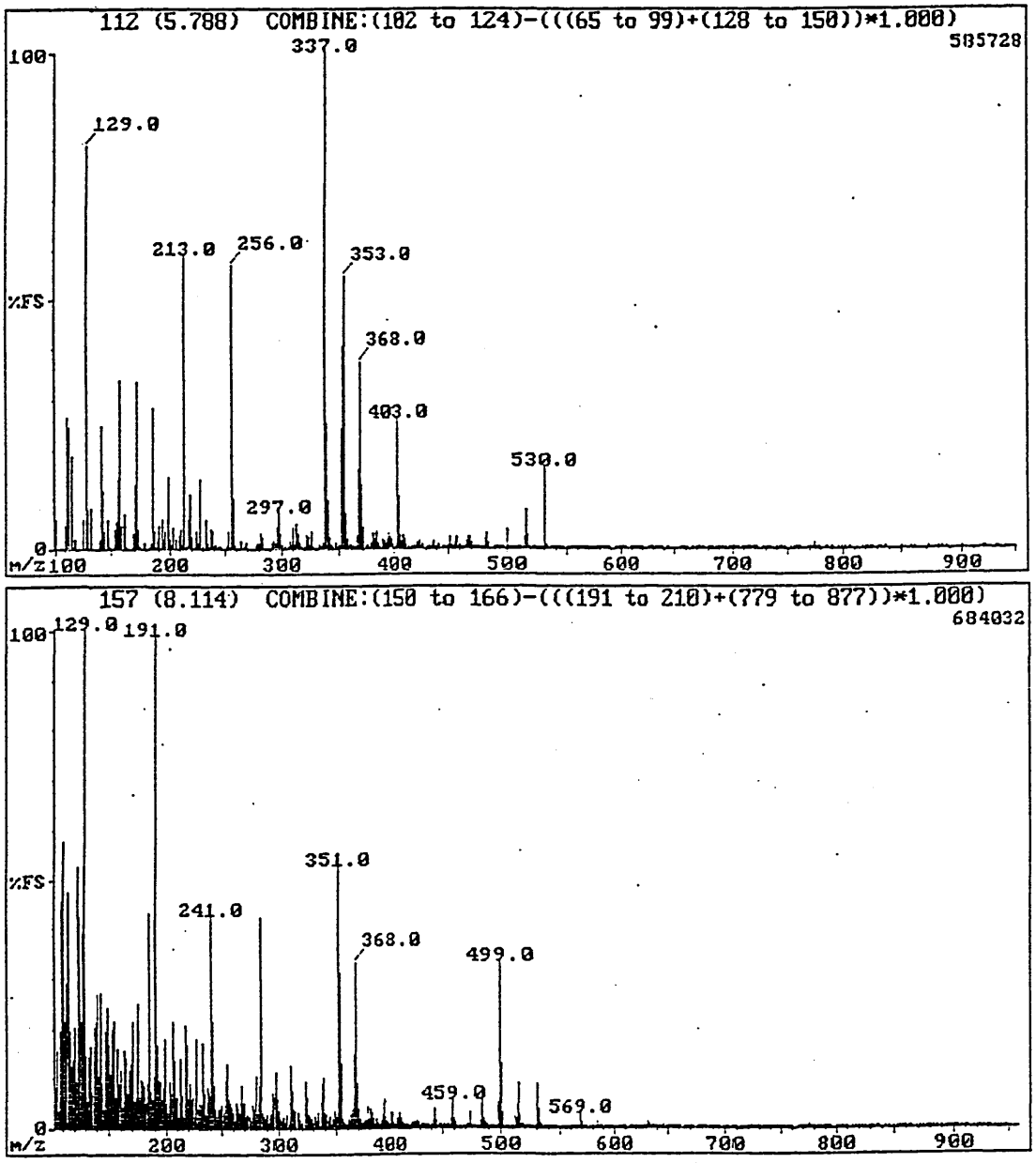


FIGURE 4.48 (A) Mass spectra obtained for some of the irradiation-derived transformation products of Irgafos 168

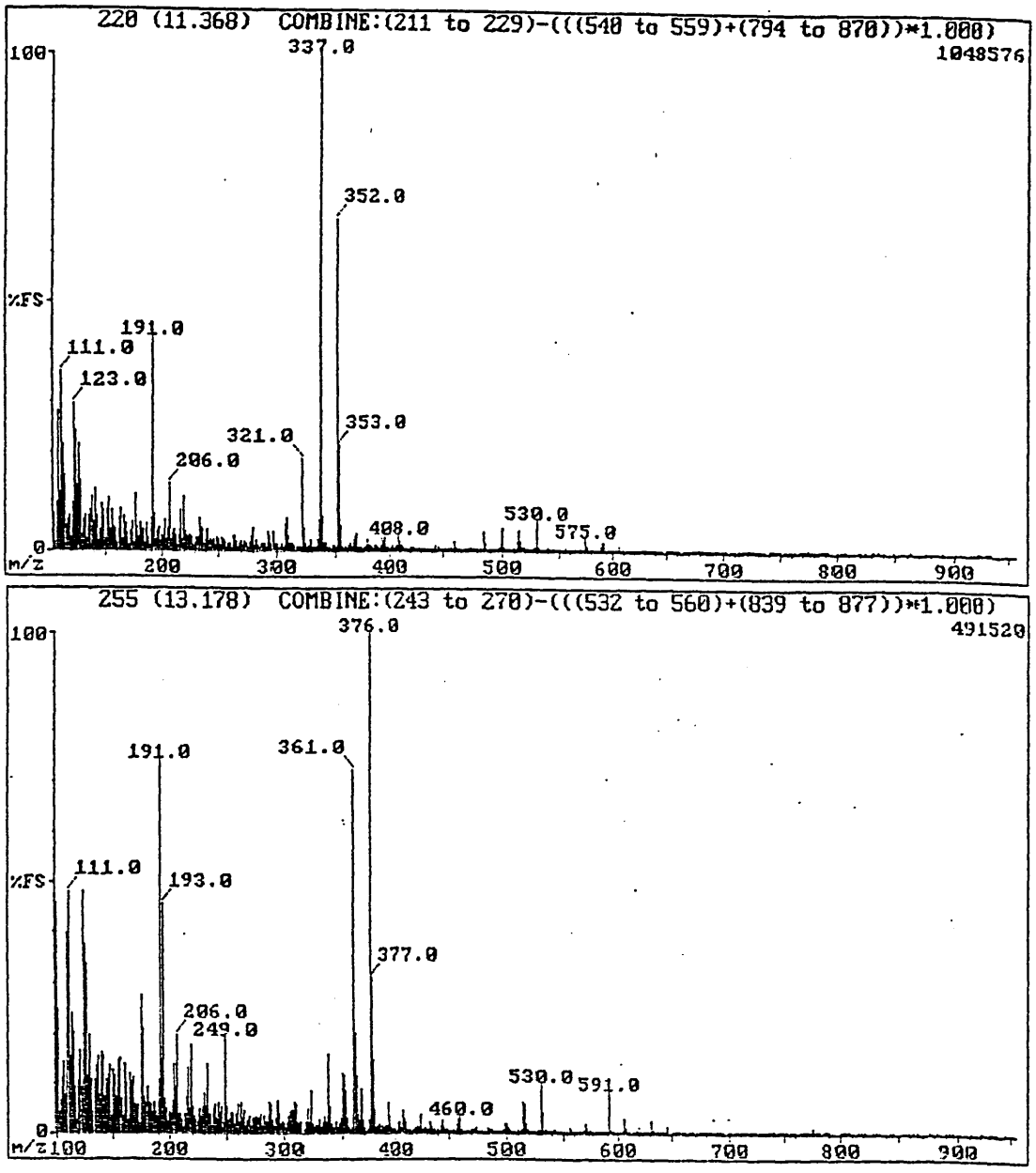

220 (11.368) COMBINE:(211 to 229)-(((540 to 559)+(794 to 870))*1.000)
100
337.0
1048576
352.0
%FS
191.0
111.0
123.0
321.0
353.0
206.0
530.0
408.0
575.0
0
m/z
200
300
400
500
600
700
800
900
255 (13.178) COMBINE:(243 to 270)-(((532 to 560)+(839 to 877))*1.000)
100
376.0
491520
191.0
361.0
%FS
111.0
193.0
377.0
206.0
249.0
530.0
591.0
460.0
0
m/z
100
200
300
400
500
600
700
800
900

FIGURE 4.48 (B)

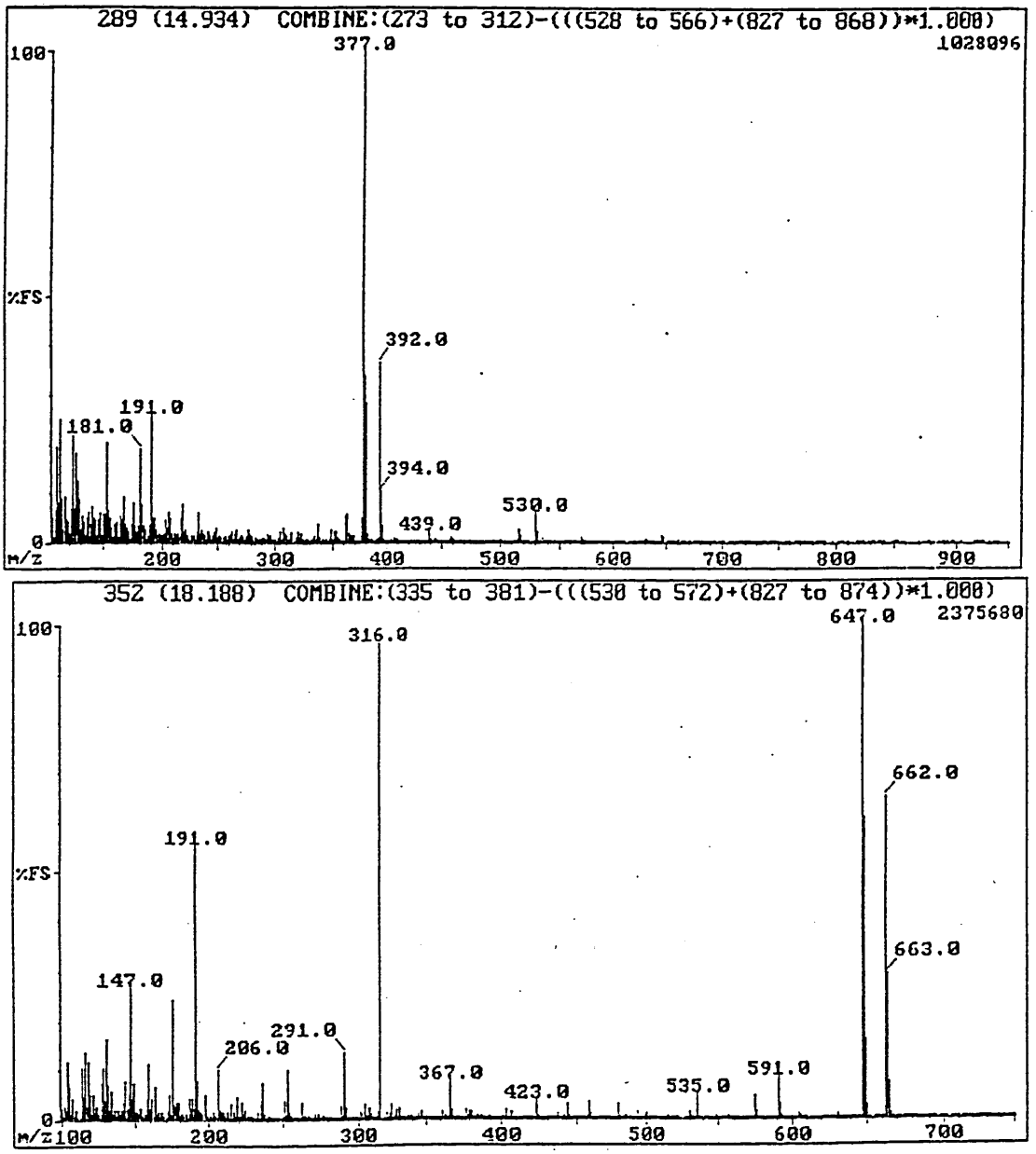

289 (14.934) COMBINE:(273 to 312)-(((528 to 566)+(827 to 868))*1.000)
1028096
100
%FS
0
m/z
377.0
392.0
191.0
181.0
394.0
530.0
439.0
200
300
400
500
600
700
800
900
352 (18.188) COMBINE:(335 to 381)-(((530 to 572)+(827 to 874))*1.000)
2375680
647.0
316.0
662.0
191.0
663.0
147.0
291.0
206.0
367.0
423.0
535.0
591.0
100

FIGURE 4.48 (C)

The extract from the sample subjected to an irradiation dose of 10kGy was also analysed using LC-MS. A number of very minor transformation products were detected along with the phosphate and an unidentified product which appears just before the phosphate, but was not clearly resolved from it and therefore did not give a mass spectrum which showed a molecular ion. The LC-MS revealed no trace of Irgafos 168 in the extract.

A sample of polypropylene stabilized by Irgafos 168 was subjected to the thermal aging process detailed in section 2.12. Separate samples were subjected to 5,9, and 16 hours respectively at 150°C in air. The samples were extracted in the usual way and chromatographed using the method detailed in section 2.8. The resulting chromatograms are displayed in figure 4.49 along with that for an extract from the untreated polymer.

The untreated sample shows the presence of Irgafos 168 at a retention time of 16 minutes 13 seconds and the presence of its related phosphate at a retention time of 7 minutes 1 second. The chromatogram also show traces of about seven other very minor products which are almost certainly present as a consequence of the initial thermal processing.

The Irganox 1010 (eluting at 10 minutes 19 seconds) is present as the internal standard.

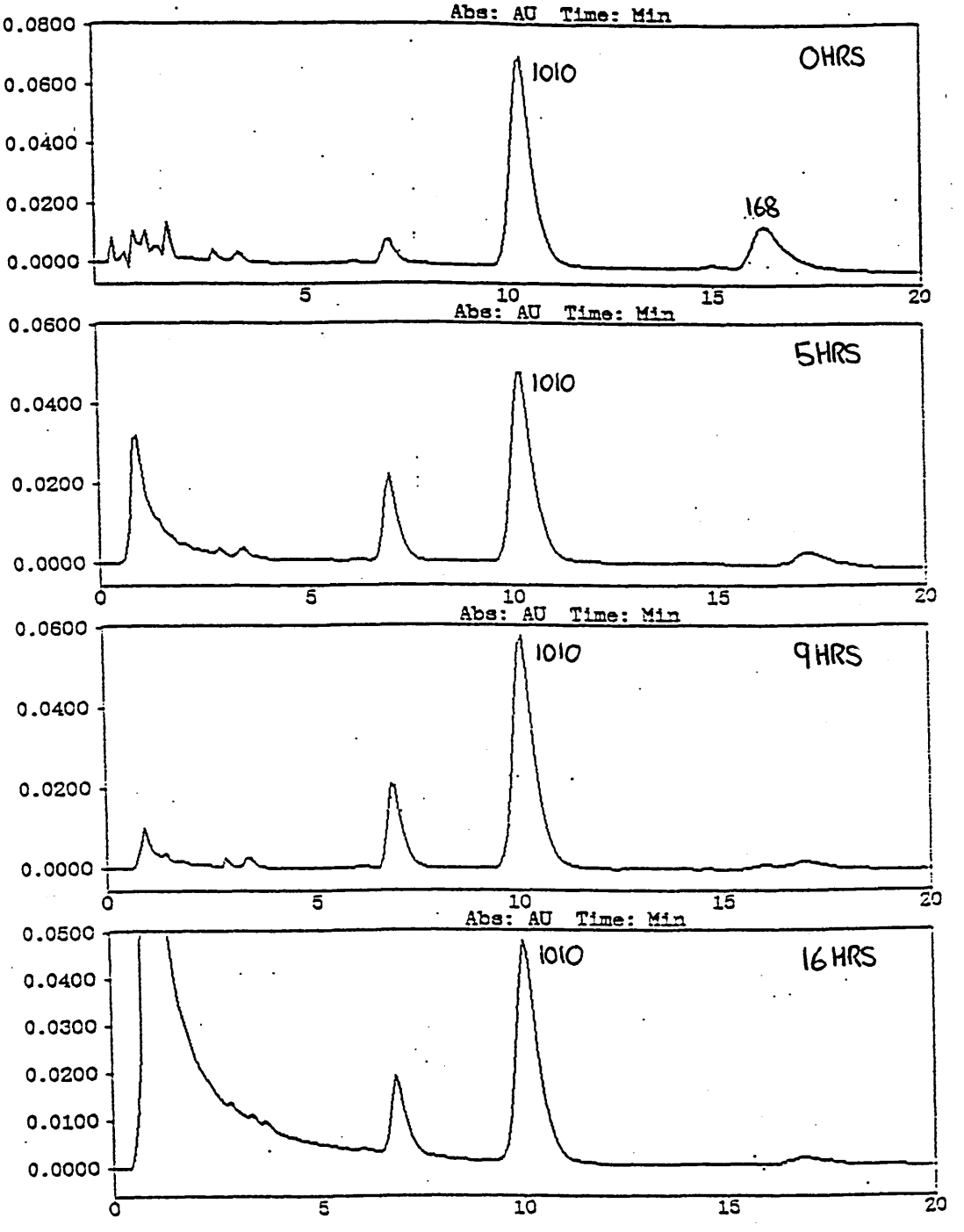


FIGURE 4.49 Isocratic hplc chromatograms for extracts from polypropylene homopolymer stabilized by Irgafos 168, after various lengths of time at 150°C in air.

After only 5 hours at 150°C in air, the Irgafos 168 is completely transformed. The height of the peak due to the phosphate increases and a new peak at 17 minutes 7 seconds appears. As the exposure time is increased further, only the peak at the solvent front increases in height. This probably indicates that Irgafos 168 is being transformed into low molecular weight polar compounds which are thus unretained by the column.

Obviously, Irgafos 168 is much less affected by irradiation than by thermal treatment and different transformation products appear to be formed depending on which process the polymer is subjected to.

A model study involving the reaction of Irgafos with t-butylperoxyl radicals was also carried out according to the method detailed in section 2.13. The resulting isocratic chromatogram is displayed in figure 4.50.

Component 2 has a UV spectrum identical to that of the phosphate derived from Irgafos 168 and component 3 has a UV spectrum identical to that of Irgafos 168 itself. The UV spectrum of the component 1 is shown in figure 4.51.

This spectrum indicates the presence of some conjugation within the structure as well as the retention of some aromatic character.

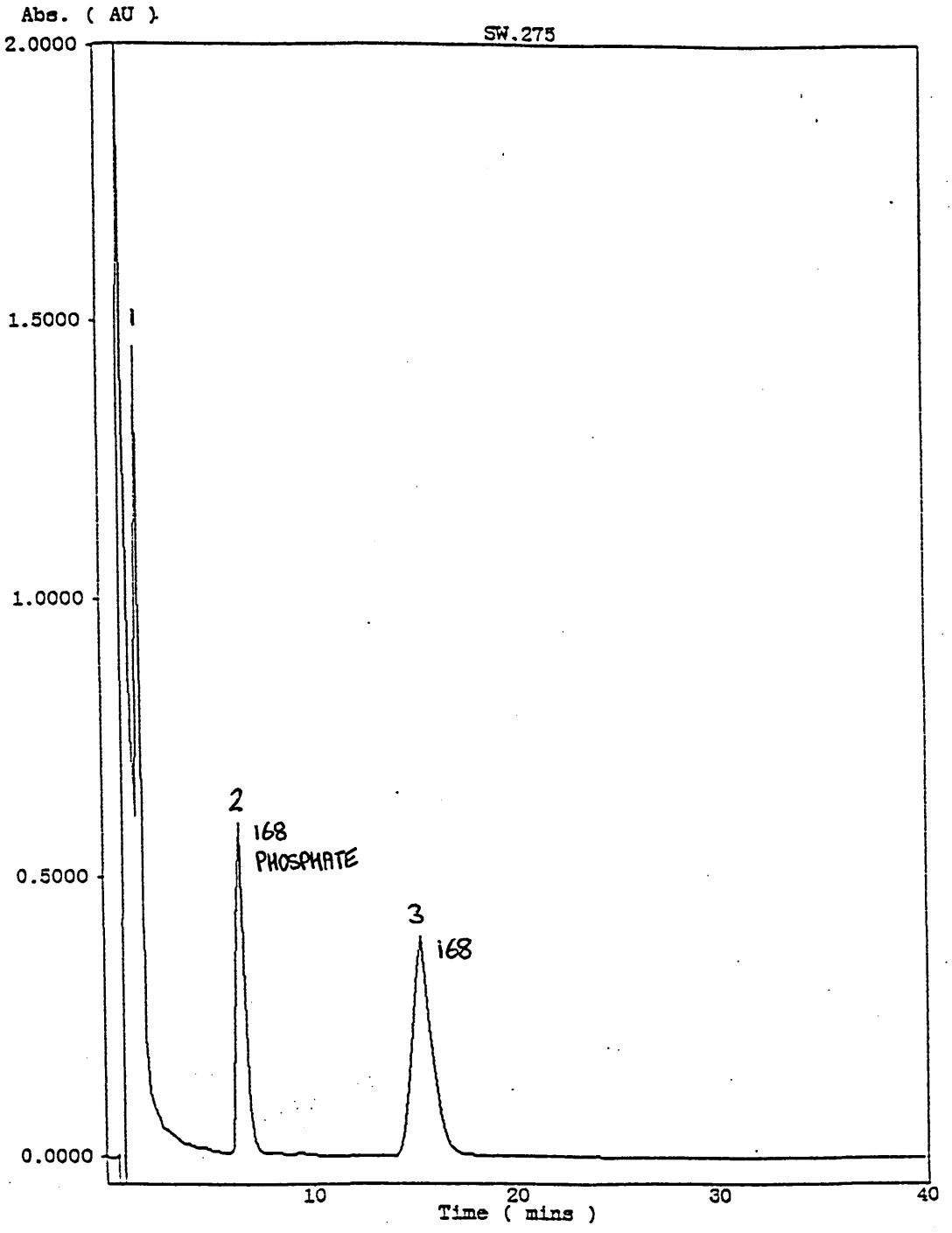


FIGURE 4.50 Isocratic hplc chromatogram obtained for the product mixture of the reaction between Irgafos 168 and t-butylperoxyl radicals.

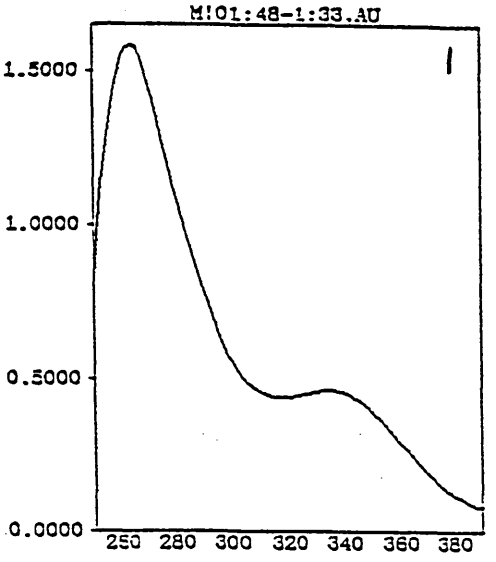
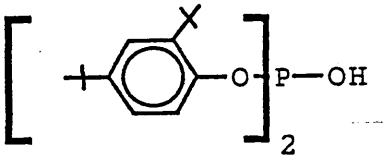


FIGURE 4.51 UV spectrum of product 1 from the reaction between Irgafos 168 and t-butylperoxyl radicals.

An LC-MS investigation of this reaction mixture revealed the presence of a further compound of relative molecular mass 458 for which the following structure was suggested.



The relative molecular mass of the previously detected compound (component 1) was found to be 502 but it remains unidentified. The presence of Irgafos 168 and its phosphate were also confirmed. The TIC is shown in figure 4.52 and the mass spectra for the two unknowns are shown in figure 4.53.

In conclusion, irradiation of polypropylene containing Irgafos 168 results in the production of many antioxidant-derived transformation products which are not produced by thermal aging of the polymer. Many of these products remain unidentified although products resulting from the cleavage of t-butyl groups again appear to be present, as with the other antioxidants. A number of the products are phosphorus-containing. The model reaction between Irgafos 168 and t-butylperoxyl radicals does not produce a similar range of compounds.

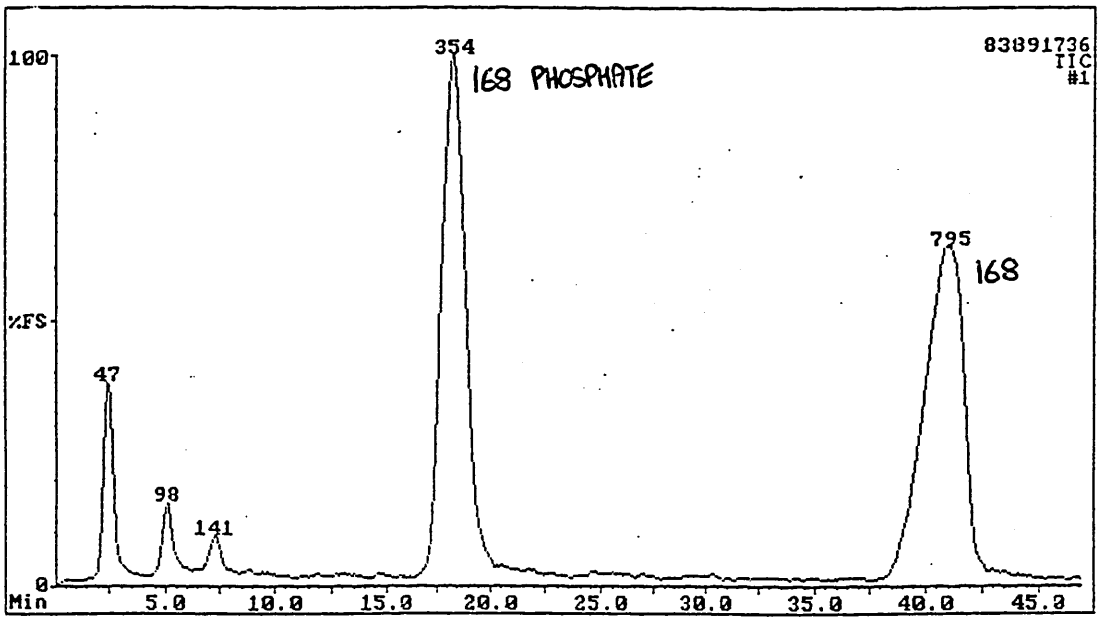


FIGURE 4.52 LC-MS TIC for the product mixture from the reaction between Irgafos 168 and t-butylperoxyl radicals.

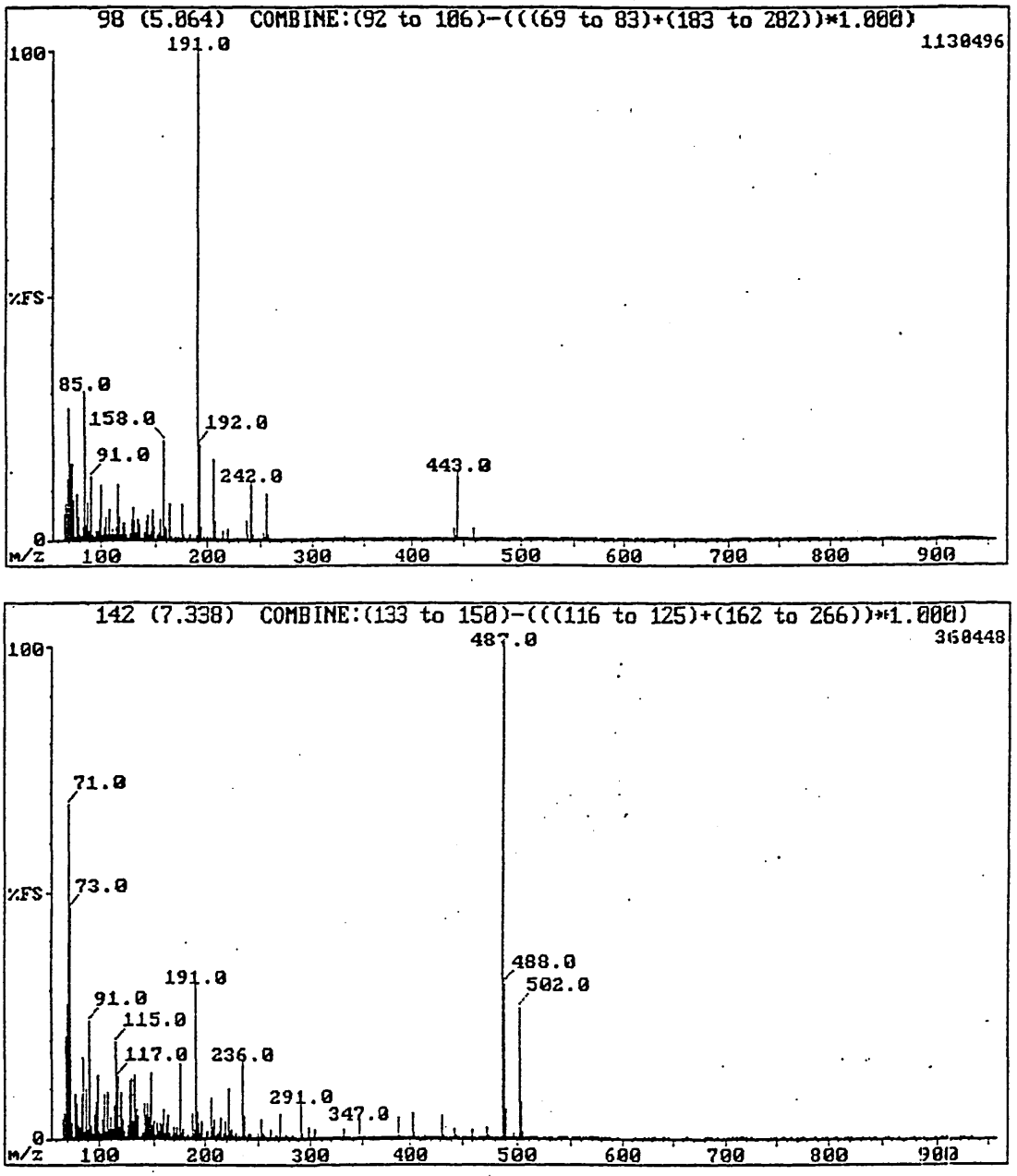


FIGURE 4.53 Mass spectra of two of the products of the reaction between Irgafos 168 and t-butylperoxyl radicals.

4.6 TRANSFORMATION PRODUCTS OF TINUVIN 622

It is not possible to readily chromatograph the polymeric hindered amine light-stabilizer, Tinuvin 622. However, it was found that the initial thermal processing to produce polypropylene beads stabilized by Tinuvin 622 results in the production of at least six transformation products which can be analysed using the hplc procedures detailed in section 2.8.

The isocratic hplc chromatogram at 275nm of the extract from polypropylene stablized by Tinuvin 622 which has not been subjected to further thermal aging or to irradiation, is displayed in figure 4.54.

This shows the presence of at least six transformation products which absorb at 275nm. This experiment was not carried out using the multichannel detector and so UV spectra were not obtained.

However, this extract was also analysed using the LC-MS technique detailed in section 2.9. The resulting total ion chromatogram is shown in figure 4.55.

The TIC shows a large number of very minor components, one prominent major component and three small but prominent peaks the first of which is distorted and impure. The mass spectra for the peaks at scan numbers 102, 133 and 366 are contained in figure 4.56. They show these compounds to have relative molecular masses of 441,279 and 663 respectively. As yet these compounds remain unidentified.

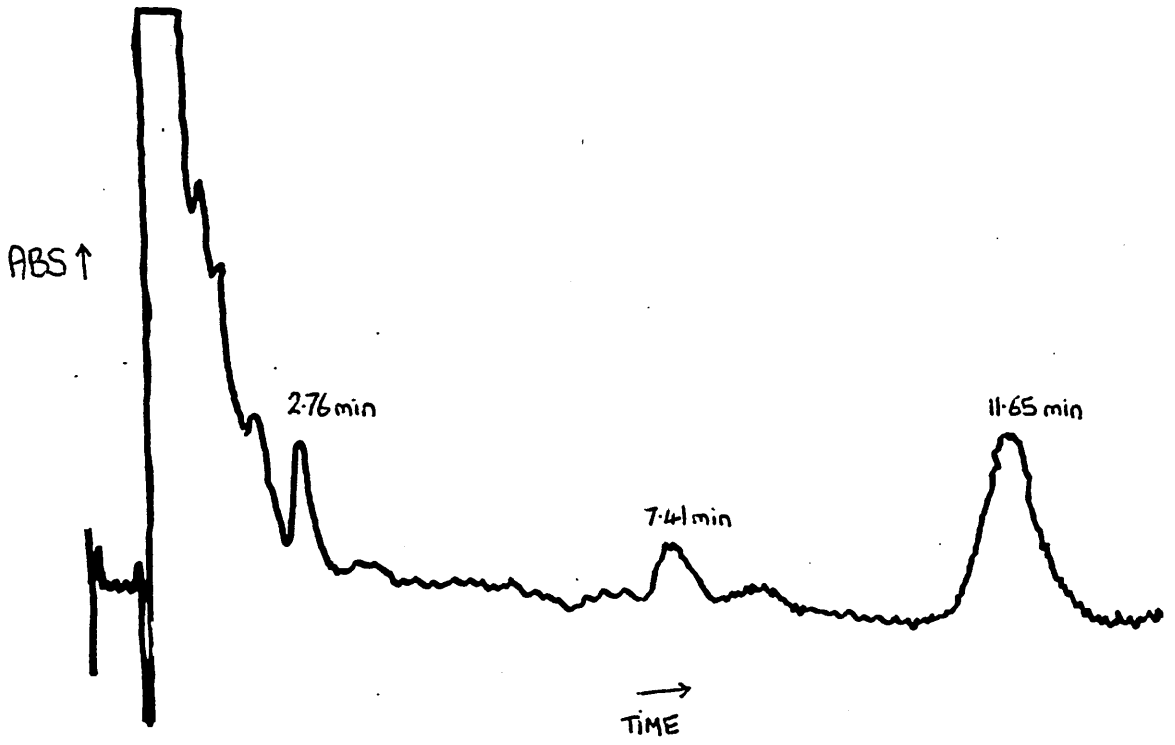


FIGURE 4.54 Isocratic hplc chromatogram of the extract from non-irradiated polypropylene homopolymer stabilized by Tinuvin 622.

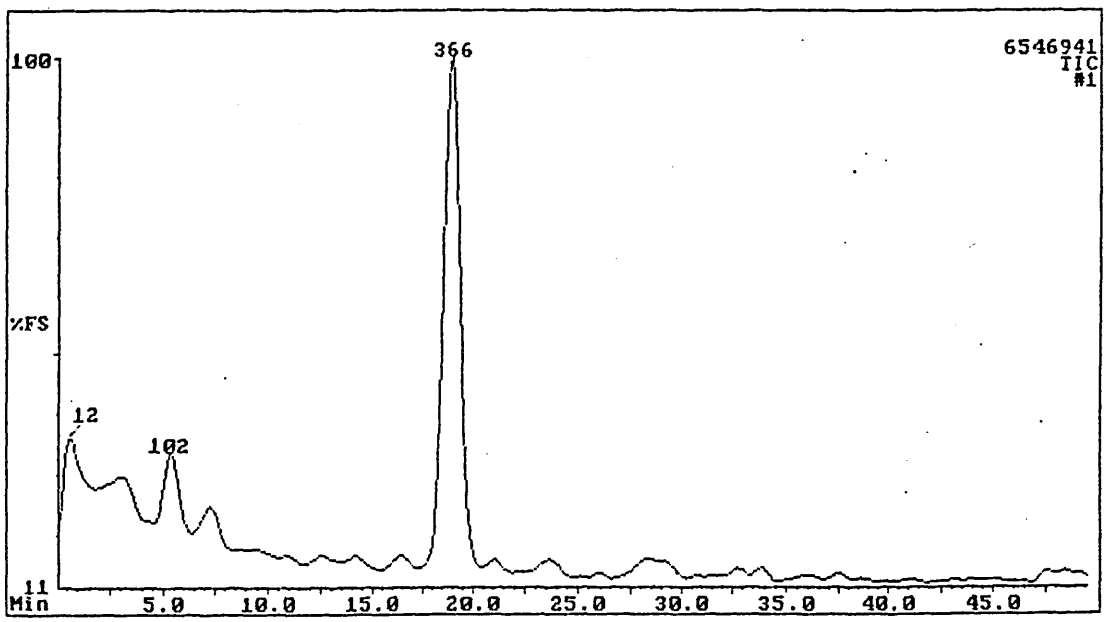


FIGURE 4.55 LC-MS TIC of the extract from non-irradiated polypropylene homopolymer containing Tinuvin 622.

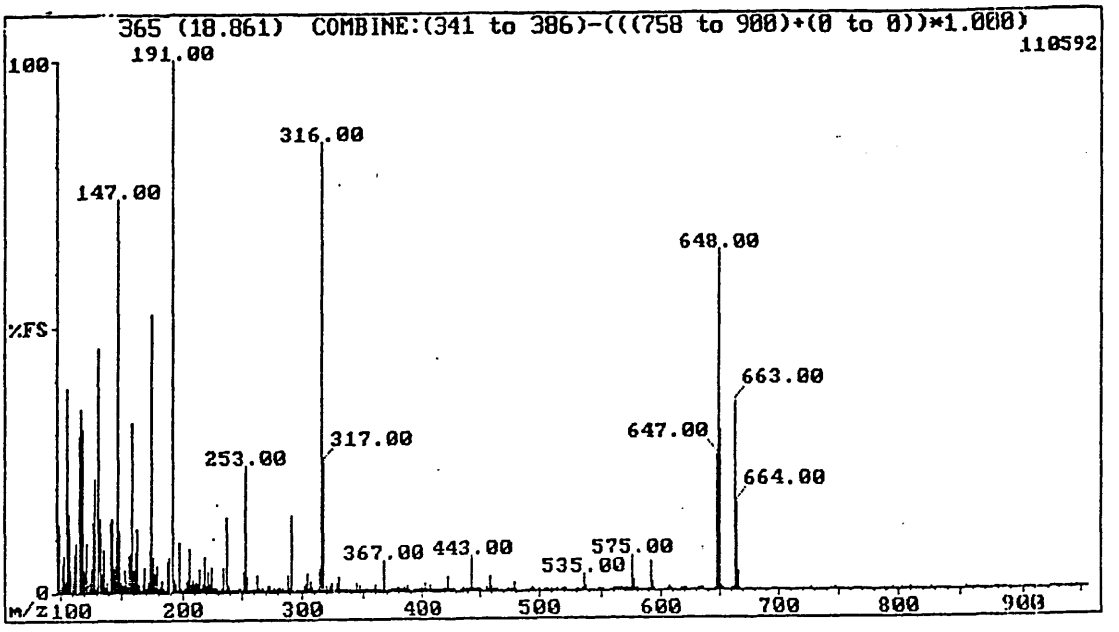


FIGURE 4.56 (A) Mass spectra of some of the thermal transformation products of Tinuvin 622.

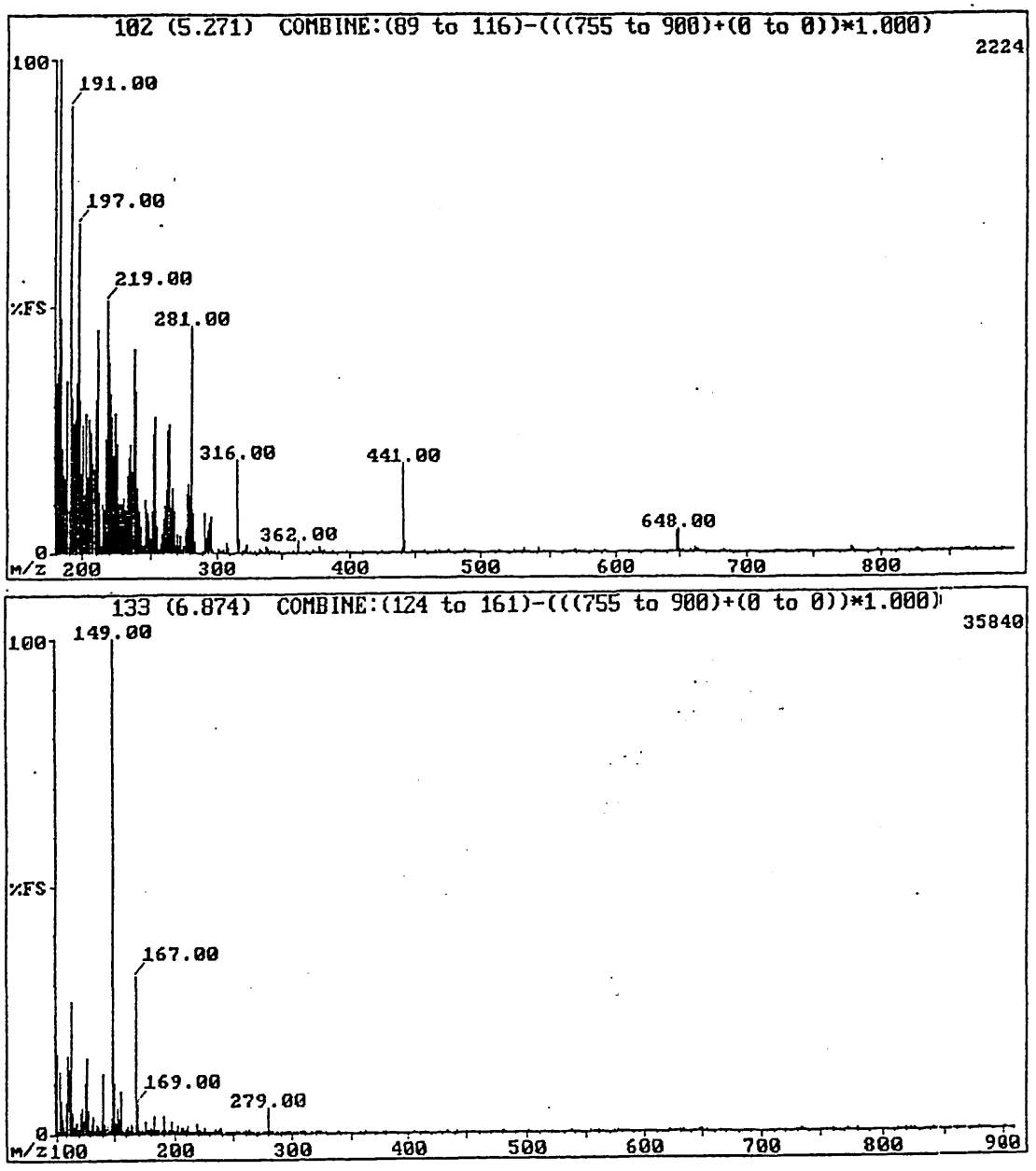

102 (5.271) COMBINE:(89 to 116)-(((755 to 900)+(0 to 0))*1.000)
2224
100
191.00
197.00
219.00
%FS
281.00
316.00
441.00
362.00
648.00
0
m/z 200 300 400 500 600 700 800
133 (6.874) COMBINE:(124 to 161)-(((755 to 900)+(0 to 0))*1.000)
35840
100
149.00
%FS
167.00
169.00
279.00
0
m/z 100 200 300 400 500 600 700 800 900

FIGURE 4.56 (B)

None of these transformation products were detectable using a 25m column for gas chromatography - mass spectrometry, and no additional products were detected. Again this implies that the transformation products are relatively involatile.

The effects of irradiation on these transformation products are detailed in section 3.5. No other transformation products, formed on irradiation of the polymer, were detected.

4.7 CONCLUSIONS

A large number of transformation products are produced by irradiation of polyolefins stabilized by the additives Irganox 1010, Irganox 1076, Irganox 1330, Irgafos 168 and Tinuvin 622, which are detectable using hplc linked to a UV/VIS multichannel detector or mass spectrometer. During this study possible structures have been suggested for many of these transformation products.

It is significant that thermal treatment or irradiation of polypropylene stabilized by the antioxidants in question may produce different products. Irradiation of the above antioxidants in polypropylene results in some cases in the loss of t-butyl groups from the parent molecules. This type of reaction seems to be unique to the irradiation process. The reactions between antioxidants and potassium hexacyanoferrate (III) or t-butylperoxyl radicals are not adequate models for the reactions occuring on irradiation of stabilized polyolefins.

Detection of many of these transformation products is not possible using gas chromatography-mass spectrometry since they appear to be of low volatility.

Hplc linked to a multichannel UV/VIS detector is a powerful tool for the detection of antioxidant transformation products and can be made even more powerful by linking to a mass spectrometer using a particle-beam interface.

The system used during this study could be improved in three ways :

a) a gradient hplc system could be used with the multichannel UV/VIS and mass spectrometry detectors.

b) the gradient hplc mobile phase could be optimized to give better resolution between the antioxidant transformation product peaks and allow more peaks to be detected in each sample during the same chromatographic run.

c) a mass spectrometer with a higher mass limit, sufficient to detect dimeric compounds could be used.

The structures proposed using UV detection and mass spectral data can be confirmed by fraction collection of the required peaks followed by nuclear magnetic resonance spectroscopy. This process must be carried out carefully, ensuring that a sufficient amount of each product is collected and all the solvents are removed before the nmr analysis. Again, this process would benefit from the use of an optimized gradient hplc system.

By combining the information gained from mass spectra, nmr spectra and UV spectra it should be possible to positively identify all the transformation products. The only limiting factor for this process is time. Unfortunately, lack of time has prevented further progress being made during the present study.

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APPENDIX 1

DETERMINATION OF ANTIOXIDANT MOLAR ABSORPTION COEFFICIENTS AT 275nm

Since 275nm has been used as the monitoring wavelength for the hplc UV detector during this study, a knowledge of the ϵ_{275nm} values for each antioxidant is important. It allows the levels of internal standard required for each analysis to be estimated more accurately. The ϵ_{275nm} were determined for each antioxidant in the following way :-

Solutions of known concentration, of the antioxidants Irganox 1010, Irganox 1076, Irganox 1330, Irganox 565 and Irgafos 168, were made up and their UV spectra were obtained using a Philips PU8720 UV/VISIBLE Scanning Spectrophotometer. Two sets of spectra were taken, one set with trichloromethane as the solvent and one set with HPLC mobile phase as the solvent. The mobile phase composition used was ethyl acetate:methanol:water 50:40:22 v/v respectively.

The absorbance readings of each antioxidant at 275nm and at λmax were measured and the molar absorption coefficients, at these wavelengths, were calculated using the formula $A=\epsilon bc$, where ϵ is the molar absorption coefficient, A is the absorbance, b is the pathlength of the cell and c is the concentration of the solution. The calculations were carried out for both solvent systems. The molar absorption coefficients and λmax values are given in tables A1 and A2.

TABLE A1

TABLE OF ANTIOXIDANT MOLAR ABSORPTION COEFFICIENTS

AT 275nm AND λmax IN TRICHLOROMETHANE

ANTIOXIDANT	λmax /nm of $CHCl_3$ solution	ε at λmax in $CHCl_3$ /m^2mol^{-1}	ε at 275nm in $CHCl_3$ /m^2mol^{-1}
IRGANOX 1010	277	758	757
IRGANOX 1076	282	257	253
IRGANOX 1330	245	765	637
IRGANOX 565	260	3729	2787
IRGAFOS 168	242	462	332

TABLE A2

TABLE OF ANTIOXIDANT MOLAR ABSORPTION COEFFICIENTS

AT 275nm AND λmax IN HPLC MOBILE PHASE

ANTIOXIDANT	λmax /nm of HPLC mobile phase solution	ε at λmax in HPLC mobile phase /m^2mol^{-1}	ε at 275nm in HPLC mobile phase /m^2mol^{-1}
IRGANOX 1010	278	671	654
IRGANOX 1076	277	172	167
IRGANOX 1330	278	583	560
IRGANOX 565	260	3452	2711
IRGAFOS 168	272	206	202

The UV cut off value for the detector when using this HPLC mobile phase is approximately 250nm. For the purpose of taking spectra, spectral subtraction was used to eliminate this effect.

The tables show that the ϵ values in HPLC mobile phase are reduced with respect to those in trichloromethane. The larger the ϵ value the lower the limit of detection will be for the antioxidant using this method.

SYMPOSIA AND MEETINGS ATTENDED

Philips Chromatography Symposium

- 19.4.89 - 20.4.89

"What can newer physical methods do for the organic chemist ?"

- A symposium organised by the SCI Fine Chemicals Group

- 13.2.90

Ministry of Agriculture, Fisheries and Food

- Working Party on chemical Contaminants from Food-Contact Materials : Project review meetings 1989, 1990 and 1991

- During the 1991 meeting the author presented a talk entitled "A comparison of the effects of gamma and electron-beam irradiation on additives present in food-contact polymers"

In addition the author attended a series of departmental research colloquia on a variety of topics.

ACKNOWLEDGEMENTS

The author would like to thank his supervisors Professor David W Allen and Dr David A Leathard for their friendship and advice throughout this investigation.

Thanks are also due to the Ministry of Agriculture, Fisheries and Food for the funding of this project and to their representatives Drs L Castle, A Smith and N J Harrison for useful discussions.

Several industrial concerns have provided materials, services or equipment during this study and the author is very grateful for this. These companies are listed below :

Viritech Limited

VG Masslab Limited

Ciba-Geigy PLC

ICI (Chemical and Polymers Group) PLC

BP Chemicals (London)

Thanks are also due to Mr K Pitcher of ICI, the industrial rapporteur throughout the study.

The author would also like to thank the staff of the Chemistry Division at Sheffield City Polytechnic, all of whom have helped him in some way throughout the project.

Finally, thanks are due to Mrs R Crowson who has patiently wordprocessed this thesis.

PUBLISHED PAPERS

During the course of this study two papers have been published. The references for these papers are given below, followed by copies of each.

D. W. Allen, A. Crowson and D. A. Leathard, *Chem. Ind. (London)*, 1990, 16-17.

D. W. Allen, A. Crowson, D. A. Leathard and C. Smith, in "Food Irradiation and the Chemist" - The proceedings of an international symposium organised by the Food Chemistry Group of the Royal Society of Chemistry as part of the Annual Chemical Congress 1990, Queen's University Belfast, 10-11 April 1990, Eds D. E. Johnston and M. H. Stevenson, Publ. Royal Society of Chemistry, 1990, p124-139.

A comparison of the effects of gamma and electron-beam irradiation on antioxidants present in food-contact polyolefins

David W Allen, Andrew Crowson and David A Leathard
Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, UK

In recent communications,[1-3] preliminary details have been reported of studies of the effects of progressive doses of gamma irradiation on the extractable levels of hindered phenol antioxidants (Irganox 1076 and Irganox 1010) and also the hindered phosphite stabiliser, Irgafos 168, present in a range of food contact polymers.

Electron-beam irradiation offers an alternative approach for the radiation treatment of pre-packaged foods as an on-line process, provided that due consideration is given to the energy of the incident radiation and to the thickness of the package. Electron-beam irradiation is carried out with high energy electron accelerators which allow the delivery of high irradiation doses over a very short period of time. Thus, whereas a typical ^{60}Co gamma source can deliver a dose rate of *ca* 12 kGy per hour, an electron beam facility can deliver several tens of kGy per second. This significant difference in dose rate might result, therefore, in changes in the chemical processes taking place in the stabilised irradiated polymer, and several groups have reported experiments which support this view. Azuma *et al*[4] have shown that electron-beam irradiation is more effective than gamma irradiation in minimising the formation of volatile degradation products derived from oxidative degradation of polyethylene. Lox *et al*[5] have discovered significant differences in the effects which gamma and electron-beam irradiation have on the extent of migration of organotin compounds from PVC into water.

Hence, it was of interest to establish whether the two irradiation processes had similar effects on the extent of destruction of antioxidants present in food contact polymers. Preliminary details are now reported of a comparison of the effects of gamma and electron-beam irradiation on the extent of destruction of Irganox 1076, Irganox 1010 and Irgafos 168 present in polypropylene and low density polyethylene (LDPE) samples.

Samples of the polyolefins stabilised as above were prepared by sintering to produce small pellets which were then subjected to progressive doses of irradiation in air from a ^{60}Co gamma source or a 4.5 MeV Dynamitron Continuous DC electron-beam facility. Following irradiation, the antioxidants were extracted from the irradiated polymers by heating under reflux in chloroform. The levels of antioxidants present in the resulting extracts were determined by HPLC techniques using appropriate internal standards (either Irganox 1076 or Irganox 1010, depending on the analyte). The results are presented in the Table.

Table Comparison of electron-beam and gamma irradiation results (percentage of initial antioxidant remaining)

Polyolefin (Per cent *w/w* of antioxidant incorporated)	Dose (KGy) / Type of irradiation	0	1	5	10	25	50
Polypropylene + 0.25 per cent Irganox 1076	Electron-beam	100	85	79	68	53	44
	Gamma	100	NA	NA	74	60	57
Polypropylene + 0.25 per cent Irganox 1010	Electron-beam	100	100	72	59	35	22
	Gamma	100	NA	NA	48	29	11
Polypropylene + 0.10 per cent Irganox 1010	Electron-beam	100	75	52	35	19	11
	Gamma	100	88	63	50	25	13
Copolymer* + 0.25 per cent Irganox 1076	Electron-beam	100	100	94	86	76	58
	Gamma	100	NA	NA	86	63	55
Copolymer* + 0.25 per cent Irganox 1010	Electron-beam	100	89	71	70	40	38
	Gamma	100	NA	NA	53	28	11
Polypropylene + 0.10 per cent Irgafos 168	Electron-beam	100	38	<16	<16	ND	ND
	Gamma	100	52	13	<13	ND	ND
LDPE + 0.20 per cent Irganox 1076	Electron-beam	100	97	88	79	59	32
	Gamma	100	100	88	81	58	35

NA = No analysis carried out; ND = not detectable; * the copolymer consists of approximately 5 per cent polyethylene in a polypropylene matrix

It is clear that there is a broad similarity in the effects of the

Contributions should have novelty and must be brief. Manuscripts must be submitted in accordance with the instructions to authors, which were published in the 6 November issue (p729). Authors are requested to note that manuscripts which do not accord with these instructions are currently being returned without consideration; in the case of overseas contributions return is by *seamail*. In order to expedite publication of accepted manuscripts, proofs are not circulated to authors outside the UK.

two types of radiation on the extent to which the above antioxidants are consumed, in the various polymer samples. With the exception of Irgafos 168, which is destroyed rapidly on irradiation, it is significant that, irrespective of the nature of the radiation employed, an appreciable proportion of the original antioxidant (*ca* 50 per cent) remains unchanged after an irradiation dose of 10kGy (1Mrad), the maximum irradiation level likely to be permitted. In its recent report, the Advisory Committee on Irradiated and Novel Foods (ACINF)[6] has advised that the irradiation of food up to an overall average dose of 10kGy presents no toxicological hazard and introduces no special nutritional or microbiological problems. The UK government has accepted the recommendations made in the ACINF report. This is likely to result in the introduction of food irradiation in the UK in the near future.

In a recent paper,[7] the authors have shown that a triazine-based hindered phenol antioxidant, Irganox 565, added as a potential internal standard in the extraction and HPLC determination of other antioxidants present in irradiated polyolefins, suffers drastic degradation as a result of rapid reactions with hydroperoxyl groups on the irradiated polymer. The possibility of a similar destruction of the internal standards used in the present study has been investigated. It is found that although there is a small degree of decomposition of the internal standards during the analytical procedure, particularly in the presence of polypropylene subjected to large doses of radiation (>25kGy), the extent of this decompostion does not introduce significant errors in the determination of the antioxidants reported in the Table.

The authors are indebted to ICI (Chemicals and Polymers Group) plc, BP Chemicals (London), and Ciba-Geigy plc for the provision of information and materials, and to Viritech Ltd (Swindon) for the use of their electron-beam irradiation facilities.

This work was supported by funds provided by the UK Ministry of Agriculture, Fisheries and Food, to whom thanks are due. The results of this work are the property of MAFF and are Crown Copyright.

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THE EFFECTS OF IONISING RADIATION ON ADDITIVES PRESENT IN FOOD-CONTACT POLYMERS

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Sheffield.
S1 1WB

1 INTRODUCTION

There is considerable current interest in the possible use of ionising radiation as a means of food preservation. Irradiation can be used to kill or reduce the numbers of pathogenic or spoilage organisms in food and to control infestation in stored products. In its recent report, the Advisory Committee on Irradiated and Novel Foods[1] (ACINF) has advised that the irradiation of food up to an overall average dose of 10 kGy presents no toxicological hazard and introduces no special nutritional or microbiological problems. The UK Government has accepted the recommendations of the ACINF report, and the introduction of food irradiation in the UK is likely in the near future.

Whereas many types of irradiated foods have been studied in depth, and the effects of irradiation on food contact plastics have been investigated in some considerable detail[2], there is much less information on the effects of irradiation on the many additives present in food-contact plastics, although it has been established that changes do occur in the migration behaviour of such additives.[3] It is possible that toxic substances might be formed within the polymer, and which could subsequently migrate into the foodstuff, thereby presenting a hazard to the consumer. In studying this area, our aims have been to study the effects of irradiation on a range of polymer-stabilising additives in terms of (i) the influence of irradiation dose on the extent of destruction of the

additive, (ii) the identification of extractable degradation products derived from the additives, (iii) the influence of irradiation dose on the extent to which the additives and their mobile degradation products are able to migrate into food-simulant media, and also (iv) to compare the effects of gamma- and electron-beam irradiation on the above.

2 RESULTS AND DISCUSSION

In early work, we showed that organotin stabilisers of the type Bu_2SnX_2 (X = $SCH_2CO_2C_8H_{17}$ or $O_2CCH{=}CHCO_2C_8H_{17}$ present in poly(vinyl chloride) (PVC) and subjected to varying doses of gamma irradiation in the range 1-200 kGy (0.1-20 Mrad) suffer degradation with dealkylation to form monobutyltin trichloride and tin(IV) chloride (Tables I and II), which have been characterised by a subsequent alkylation procedure followed by gas chromatographic analysis. The extent of degradation of the stabilisers on prolonged gamma irradiation is much more severe than during thermal degradation leading to comparable blackening of the polymer.[4-7]

Table I Analysis of Gamma-Irradiated PVC Samples containing dibutyltin bis(iso-octylthioglycollate) (1.2% w/w [$Bu_2Sn(IOTG)_2$]

Exposure (kGy)	Relative proportion of degradation products[a] (%)		
	Bu_2SnX_2	$BuSnX_3$	$SnCl_4$
0	92	6	2
5	87	10	3
10	88	7	5
15	75	15	10
20	72	17	11
25	70	16	14
50	52	14	34
100	35	18	47
200	15	17	68

[a]X = $SCH_2CO_2C_8H_{17}$ or Cl

Table II Analysis of Gamma-Irradiated PVC Samples (Milled) containing Dibutyltin bis(iso-octylmaleate) (2% w/w) [$Bu_2Sn(IOM)_2$]

Exposure (kGy)	Relative proportion of degradation products[a] (%)		
	Bu_2SnX_2	$BuSnX_3$	$SnCl_4$
0	97	3	1
5	91	5	4
10	90	7	3
15	92	4	4
20	92	4	4
25	89	6	5
50	68	16	16
100	59	22	19
200	41	17	42

[a]X = $O_2CCH{=}CHCO_2C_8H_{17}$ or Cl

In more recent work, we have studied the fate of hindered phenol and arylphosphite antioxidants (e.g. Irganox 1076, 1010, and 1330, and Irgafos 168) (Scheme 1) present in a range of polymers, including PVC, polyethylene and polypropylene which have been subjected to varying doses of gamma- and electron beam-irradiation. Such antioxidants are present not only to stabilise the polymer during initial processing and fabrication, but also during subsequent service, their main role being the removal of alkoxy and alkylperoxo radicals which would otherwise lead to degradation of the polymer. These compounds would be expected to have an important role to play in the suppression of the ambient-temperature oxidation of polyolefins following irradiation.[8-11]

Our hplc analytical results revealed the progressive destruction of the antioxidants on gamma-irradiation, the rate of loss depending on the nature of both antioxidant and base polymers (Tables III and IV). In most cases, a significant (but not drastic) loss of antioxidant (ca. 30%) occurs on exposure to a gamma irradiation dose of 10 kGy (1 Mrad), the maximum dose likely to be permitted should food irradiation gain general approval in the UK. Reanalysis of the polymers after a six-month interval has revealed little

subsequent post-irradiation degradation of the antioxidants. The extent of degradation of the antioxidants after a 25 kGy dose is correspondingly greater.[12]

Table III Effects of Gamma-irradiation on Phenolic Antioxidants Present in poly(vinyl chloride), polyethylene and polypropylene

	PVC		Polyethylene		Polypropylene	
Irradiation Dose/kGy	Irganox 1076[a]	Irganox 1010[b]	Irganox 1076[a]	Irganox 1010[b]	Irganox 1076[a]	Irganox 1010[b]
0	0.44	0.62	0.36	0.16	0.34	0.08
1	0.29	0.46	0.28	0.12	0.37	0.07
5	0.27	0.46	0.23	0.10	0.38	0.05
10	0.12	0.43	0.22	0.09	0.38	0.04
20	0.17	0.37	0.20	0.07	0.36	0.02
25	0.18	0.31	0.14	0.07	0.35	0.02
35	0.19	0.30	0.14	0.05	0.30	0.01
50	0.15	0.24	0.11	0.04	0.30	0.01

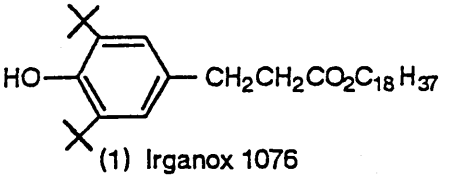
[a]±0.03%. [b]±0.01%.

Table IV Effects of Gamma-irradiation on Irgafos 168 Present in Polypropylene

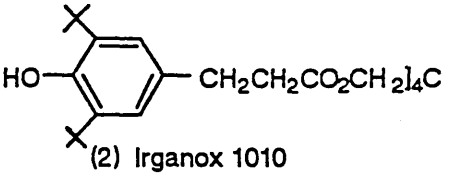
	Irgafos 168 as sole antioxidant %	Combination of Irgafos 168 + Irganox 1010 %	%
Irradiation Dose/kGy	Irgafos 168[a]	Irgafos 168[a]	Irganox 1010[b]
0	0.067	0.069	0.08
1	0.035	0.010	0.05
5	0.009	-	0.04
10	0.004	-	0.03
20	-	-	0.02
25	-	-	0.01

[a]±0.003. [b]±0.01.

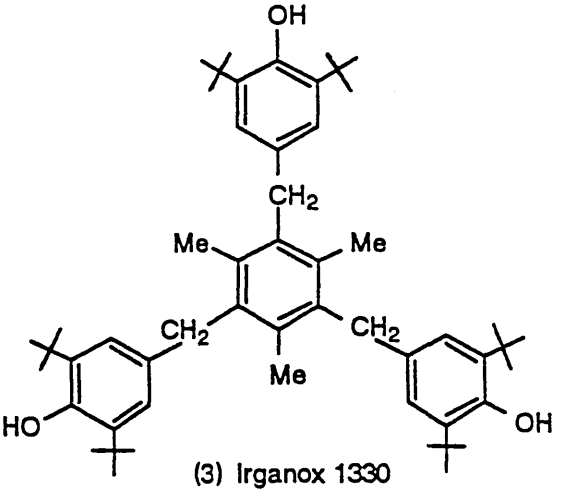
In the case of the hindered phenol antioxidants, we did not initially detect significant quantities of degradation products which could be extracted from the irradiated polymer, and it was suspected that such products were becoming covalently bound to the polymer as a result of radical coupling processes. It has recently been shown that gamma-irradiation of hindered phenols in benzene solution gives rise to phenylated derivatives resulting from coupling of radicals derived from the antioxidants with phenyl radicals derived from the solvent.[13] Gamma-irradiation of polyolefins



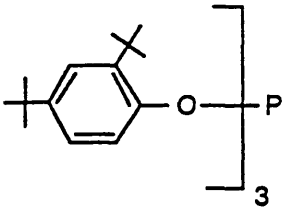
(1) Irganox 1076



(2) Irganox 1010



(3) Irganox 1330



(4) Irgafos 168

(Scheme 1)

is known to give rise to macroalkyl radicals, and hence the trapping of antioxidant degradation products is therefore probable. If this is so, then concerns over the migration of potentially toxic degradation products are much reduced.

Experiments involving a ^{14}C-labelled antioxidant in irradiated polyolefins have given some support to this suggestion. A sample of Irganox 1076 labelled with ^{14}C at the benzylic carbon of the arylpropionic acid moiety was diluted with unlabelled Irganox 1076, and the diluted, labelled antioxidant incorporated into both polypropylene and high density polyethylene at ca. 0.2% by weight. Following irradiation, the total extractable ^{14}C-activity was measured, and found to decline progressively as the irradiation dose increased for both polymer systems. At the same time, the residual ^{14}C-activity of the exhaustively-extracted polymers was found to increase with increasing dose, indicating the probable binding of at least 20% of the total available ^{14}C-activity to the polymer after a 50 kGy exposure. In order to explore the possibility of physical entrapment of antioxidant and degradation products in the possibly cross-linked, irradiated polymer, which could, in itself, result in the observed reduction in extractable radioactivity, a 50 kGy-irradiated sample of the ^{14}C-labelled polypropylene was dissolved in hot tetralin, followed by precipitation of the polymer by the addition of hexane. It was considered that any unbound antioxidant (and degradation products) would be removed in the tetralin fraction, whereas the bound substances would be precipitated with the polymer. The precipitated polymer fraction was repeatedly washed with hexane to remove any residual unbound activity, and its ^{14}C-activity then assayed. The results of this procedure indicated that at least 12.4% of the total ^{14}C-activity had become polymer-bound as a result of the irradiation process. The true figure is likely to be significantly higher (as indicated by the above residual activity figure), as a result of losses of labelled low molecular weight oligomeric fractions into the supernatant liquid in the above dissolution-precipitation procedure. This investigation could not be repeated using high density polyethylene because, following irradiation, this material became impossible to dissolve in hot tetralin, presumably as a result of cross-linking. Thus, although evidence of binding of antioxidant-degradation products to the irradiated

polymer has been obtained, the extent of the binding is lower than might have been expected in view of our initial failure to detect extractable degradation products by HPLC techniques. In subsequent studies, we have now refined our chromatographic procedures, and have observed a number of extractable degradation products arising from the above range of hindered phenol antioxidants. Thus, in the case of Irganox 1076, one significant degradation product has been detected, whereas for Irganox 1010, three major and several minor degradation products have been detected. Similarly, for Irganox 1330, several degradation products are apparent. The challenge now is to isolate and characterise these substances.

In the case of the arylphosphite stabiliser, Irgafos 168, we have shown that drastic reductions in the level of the antioxidant occur during gamma irradiation, to such an extent that little remains after a dose of 10 kGy (Table IV). In addition, we have detected the triarylphosphate oxidation product of Irgafos 168 in the extracts of the irradiated polymers by both hplc and ^{31}P nmr techniques. As the irradiation dose increases, it would appear that the phosphorus-containing degradation products are also becoming covalently bound to the polymer. However, there is also evidence of the formation of a range of extractable degradation products in increasing amounts as the dose increases.

We have also studied the effects of gamma irradiation on the extent of migration of hindered phenol antioxidants into fatty food simulants.[14] It is generally considered that the migration of polymer additives into foodstuffs is a diffusion problem, and depends on many variables.[15] As the determination of migrated polymer additives in heterogeneous foodstuffs is a difficult and time-consuming task, it has become common practice to study the migration of polymer additives into a series of homogeneous liquid, food simulant media under standard conditions, e.g. a polymer surface area of 2 dm^2 exposed to 100 cm^3 simulant over a period of 10 days at 40 °C. A range of oily, alcoholic and aqueous simulants specified by EEC Directive,[16] has been widely used in such studies.

The specific systems studied by us to date have involved the migration of Irganox 1076 and Irganox 1010 present in polyolefins into the synthetic triglyceride

fatty food simulant HB307 (10 days at 40 °C), and, for comparison, into iso-octane (2 days at 20 °C). The latter has been proposed[17] as a fatty food simulant which provides a convenient alternative to fats such as HB307 and olive oil in that determination of migration into iso-octane is significantly easier, thereby providing a fast, cheap and simple predictive method for assessment of migration into fatty media. However, criticisms have been made of the use of iso-octane for this purpose.[18,19]

Samples of polypropylene in sheet form, containing Irganox 1076 and 1010, respectively at ca. 0.2% by weight, were prepared by conventional hot-milling and compression moulding techniques. These were used in studies of the extent of migration into iso-octane at 20 °C over 2 days, the antioxidants being determined by hplc techniques. For studies of migration into the synthetic fat HB307 at 40 °C over a period of 10 days, a ^{14}C-labelled Irganox 1076 antioxidant was similarly incorporated into both polypropylene and high density polyethylene. The extent of migration was assayed by conventional liquid scintillation techniques. In separate experiments, it was demonstrated by TLC techniques that the ^{14}C-activity migrating into the simulant was due predominantly to unchanged ^{14}C-labelled Irganox 1076, although small amounts of another, as yet unidentified substance could also be detected. We therefore feel justified in assuming that the ^{14}C-activity of the simulant reflects the degree of migration of the antioxidant. Prior to the migration experiment, the polymer samples were subjected to varying doses of gamma-irradiation from a Cobalt-60 source. The results of the migration experiments are presented (Table V) as specific migration values (mg antioxidant migrated per dm^2 contact area).

It is clear that the extent of migration into the iso-octane and HB307 decreases steadily as irradiation progresses, consistent with the reduction in the amount of extractable antioxidant revealed in our earlier study.[12] These results are also consistent with an earlier report[20] of the effects of a 25 kGy gamma dose on the migration of Irganox 1076 into HB307. It is of interest that the extent of migration of Irganox 1076 into iso-octane is significantly greater than that of Irganox 1010 reflecting the greater lipophilicity of the former. Furthermore, while the extent of migration

of Irganox 1076 into iso-octane is greater than into HB307 under the stated conditions, the results are nevertheless comparable in magnitude, thus providing some justification for the use of iso-octane as a convenient indicator simulant for migration into fatty foods. The key conclusion from our study, however, is that gamma irradiation leads to a decrease in the degree to which hindered phenol antioxidants migrate from polyolefins into fatty media.

Table V Effects of Gamma Irradiation on Migration of Antioxidants into Fatty Food Simulants

	Iso-octane		HB307 ^{14}C-Irganox 1076	
Irradiation Dose/kGy	Irganox 1076 mg dm^{-2} polypropylene	Irganox 1010 mg dm^{-2} polypropylene	mg dm^{-2} polypropylene	mg dm^{-2} HDPE
0	2.6	0.8	1.0	1.3
10	2.1	0.3	0.7	1.0
25	1.3	<0.2	0.5	0.7
50	0.4	<0.2	0.2	0.3

Electron-beam irradiation offers an alternative approach for the radiation treatment of pre-packaged foods as an on-line process, provided that due consideration is given to the energy of the incident radiation and to the thickness of the package. Electron-beam irradiation is carried out with high energy electron accelerators which allow the delivery of high irradiation doses over a very short period of time. Thus, whereas a typical ^{60}Co gamma source can deliver a dose rate of *ca* 12 kGy per hour, an electron beam facility can deliver several tens of kGy per second. This significant difference in dose rate might result, therefore, in changes in the chemical processes taking place in the stabilised irradiated polymer, and several groups have reported experiments which support this view. Azuma *et al*[21] have shown that electron-beam irradiation is more effective than gamma irradiation in minimising the formation of volatile degradation

products derived from oxidative degradation of polyethylene. Lox *et al*[22] have discovered significant differences in the effects which gamma and electron-beam irradiation have on the extent of migration of organotin compounds from PVC into water.

Hence, it was of interest to establish whether the two irradiation processes had similar effects on the extent of destruction of antioxidants present in food contact polymers. Preliminary details have been reported of a comparison of the effects of gamma and electron-beam irradiation on the extent of destruction of Irganox 1076, Irganox 1010 and Irgafos 168 present in polypropylene and low density polyethylene (LDPE) samples.[23]

Samples of the polyolefins stabilised as above were prepared by sintering to produce small pellets which were then subjected to progressive doses of irradiation in air from a ^{60}Co gamma source or a 4.5 MeV Dynamitron Continuous DC electron-beam facility. Following irradiation, the antioxidants were extracted from the irradiated polymers by heating under reflux in chloroform. The levels of antioxidants present in the resulting extracts were determined by HPLC techniques using appropriate internal standards (either Irganox 1076 or Irganox 1010, depending on the analyte). The results are presented in Table VI.

It is clear that there is a broad similarity in the effects of two types of radiation on the extent to which the above antioxidants are consumed, in the various polymer samples. With the exception of Irgafos 168, which is destroyed rapidly on irradiation, it is significant that, irrespective of the nature of the radiation employed, an appreciable proportion of the original antioxidant (*ca* 50 per cent) remains unchanged after an irradiation dose of 10 kGy (1 Mrad), the maximum irradiation level likely to be permitted. In addition, a comparison of the chromatograms obtained from the extracts of both gamma- and electron beam-irradiated polymers also reveals a very similar pattern of degradation products arising from a given antioxidant.

A preliminary study of the extent of migration of Irganox 1076 into iso-octane from a polypropylene-polyethylene copolymer subjected to electron-beam irradiation, together with corresponding data for the

gamma-irradiated material, also reveals a broadly similar situation (Table VII). It is of interest that these results for the copolymer are noticeably higher than those for polypropylene presented earlier (Table V).

Table VI Comparison of electron-beam and gamma-irradiation results (percentage of initial antioxidant remaining)

Polyolefin (Per cent w/w of antioxidant incorporated)	Type of irradiation	Dose (kGy) 0	1	5	10	25	50
Polypropylene +0.25 per cent Irganox 1076	Electron-beam	100	85	79	68	53	44
	Gamma	100	NA	NA	74	60	57
Polypropylene +0.25 per cent Irganox 1010	Electron-beam	100	100	72	59	35	22
	Gamma	100	NA	NA	48	29	11
Polypropylene +0.10 per cent Irganox 1010	Electron-beam	100	75	52	35	19	11
	Gamma	100	88	63	50	25	13
Copolymer* +0.25 per cent Irganox 1076	Electron-beam	100	100	94	86	76	58
	Gamma	100	NA	NA	86	63	55
Copolymer* +0.25 per cent Irganox 1010	Electron-beam	100	89	71	70	40	38
	Gamma	100	NA	NA	53	28	11
Polypropylene +0.10 per cent Irgafos 168	Electron-beam	100	38	<16	<16	ND	ND
	Gamma	100	52	13	<13	ND	ND
LDPE +0.20 per cent Irganox 1076	Electron-beam	100	97	88	79	59	32
	Gamma	100	100	88	81	58	35

NA = No analysis carried out; ND = not detectable; *the copolymer consists of approximately 5 per cent polyethylene in a polypropylene matrix.

In the course of the above studies of the fate of antioxidants present in food-contact polymers subjected to varying irradiation doses, we have developed hplc procedures for individual antioxidants, e.g. Irganox 1076, which have involved the use of one of the related antioxidants e.g. Irganox 1010, as an internal standard. However, for the determination of Irgafos

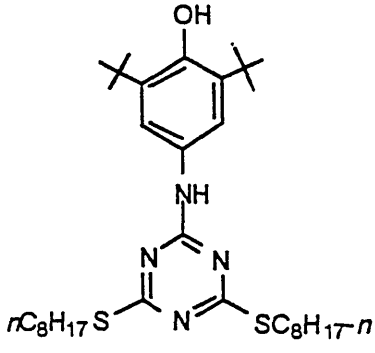
Table VII Comparison of the Effects of Gamma- and Electron-Beam Irradiation on Migration of Irganox 1076 from a Polypropylene-Polyethylene Copolymer into Iso-octane (2 days at 20 °C)

Dose (kGy)	Electron Beam Irradiation mg dm^{-2}	Gamma Irradiation mg dm^{-2}
0	3.7	5.1
10	2.8	4.3
25	2.2	2.7
50	1.6	1.3

168 in the presence of Irganox 1010 in synergistically-stabilised systems, it was necessary to seek an alternative internal standard, and the triazine, Irganox 565, 2,4-bis(*n*-octylthio)-6-(4-hydroxy-3,5-di-*t*-butylphenylamino)-1,3,5-triazine (5) was selected because of its favourable retention behaviour relative to the two analytes under the conditions employed. In the analytical procedure, samples of polymer were extracted under reflux in chloroform, which had been spiked with Irganox 565 as internal standard. In the analysis of unirradiated, thermally processed polypropylene, Irganox 565 functioned as a perfectly acceptable internal standard. However, when applied to samples of gamma-irradiated polypropylene and low density polyethylene (LDPE), it was found that the internal standard was progressively destroyed during the reflux period.[24]

In the case of polypropylene which had received a dose of 1 kGy, the Irganox 565 was completely destroyed. With gamma-irradiated LDPE, the rate of destruction was slower but significantly dose-related,

complete destruction only being observed after a dose of 50 kGy. In contrast, little degradation was observed in the presence of irradiated high density polyethylene (HDPE). Investigation of the behaviour of Irganox 565 in the presence of gamma-irradiated-polypropylene or -LDPE, containing no other antioxidants, revealed that it is converted into the iminoquinone (6), identified by comparison with the authentic material prepared by oxidation of the triazine (5) with manganese dioxide in chloroform at room temperature.



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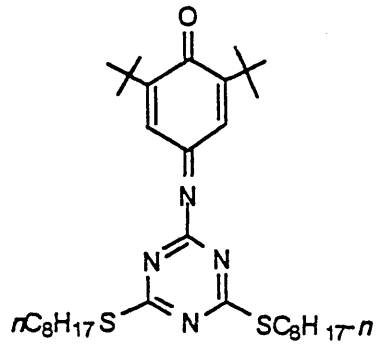

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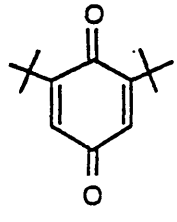

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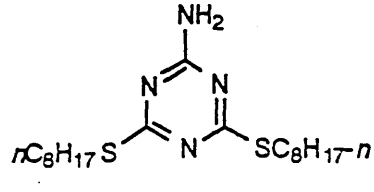

(8)

It is likely that the iminoquinone (6) is formed from the reactions of Irganox 565 with hydroperoxo groups formed at tertiary carbon sites in the irradiated polymers. Although hydroperoxides are formed during the thermal processing of polymers, it is clear that a much greater number of such groups are formed during gamma-irradiation in air. As pointed out above, little degradation of Irganox 565 occurs in the presence of an unirradiated (but thermally processed) polyolefin. The significantly smaller number of easily

peroxidisable sites in irradiated HDPE doubtless accounts for the much reduced rate of destruction of the triazine (5). We have carried out model studies of the reaction of compound (5) with *t*-butyl hydroperoxide in chloroform solution, showing that the iminoquinone (6) is readily formed, together with the quinone (7) and the aminotriazine (8), arising from the hydrolysis of the iminoquinone (6) by traces of water in the peroxide reagent.

A very similar state of affairs applies to the decomposition of Irganox 565 by electron beam-irradiated polymers, the extent of decomposition again increasing from HDPE to LDPE to polypropylene. In all cases, the effect is dose-related.

In view of these findings, the possibility of a similar destruction of other internal standards used in the determination of antioxidants in irradiated polymers has also been investigated. It is found that although there is a small degree of decomposition of both Irganox 1076 and Irganox 1010 when used as internal standards, particularly in the presence of polypropylene subjected to large doses of irradiation (>25 kGy), the extent of this decomposition does not induce significant errors in the determination of the antioxidants discussed above. However, this study has indicated that Irgafos 168 is also rapidly destroyed when heated in solution in the presence of irradiated polymers. Similarly, Irganox 1330 is also subject to destruction at a similar rate to Irganox 565. Hence, in the determination of antioxidants in irradiated polymers, it is essential to select an internal standard which is relatively stable under the conditions employed. An additional problem is the related destruction of the analyte during solvent extraction from the irradiated polymer. An ideal internal standard for a given antioxidant analyte would therefore be a substance which suffers degradation at about the same rate as the analyte. Clearly, there are many challenges to the analytical chemist in this field!

As this Conference has shown, there is considerable interest in the development of tests for irradiated food. The above, "unexpected" chemistry may indicate an alternative approach in that it may be possible to devise reagents which would reveal whether a food-contact plastic has been irradiated.

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